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Unprecedented CO_2-Promoted Aminochlorination of Olefins with Chloramine-T

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ABSTRACT

A new synthetic procedure for the aminochlorination of olefins for the synthesis of vicinal chloroamine derivatives using a combination of Chloramine-T and carbon dioxide is described. The method can be applied to a variety of olefins, including an electron-sufficient olefin and a conjugated diene.

Vicinal haloamine derivatives are versatile synthetic intermediates for the synthesis of functional materials and biologically active compounds.[1] Among the synthetic routes to these 1,2-haloamines, the direct 1,2-functionalization of olefins is a practical method, due to the fact that the starting materials are readily available olefins. Although noncatalytic procedures for the preparation of 1,2-haloamines by the addition of *N*-halo derivatives to olefins have been reported, these processes suffer from low efficiency.[2]

Li[3] and Sudalai[4] and other groups[5] recently reported on the elegant aminohalogenation of olefins catalyzed by transition metal salts using an *N*,*N*-dichlorosulfonamide or a combination of a sulfonamide and NBS. In our[6a−f] continuing efforts to provide new methods for synthesis of

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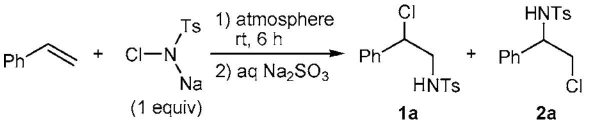
N-heterocycles,[6g] the inexpensive Chloramine-T (CT)[7] is found to be a good N_1 unit. A few examples of the aminohalogenation of olefins with CT have been reported, but the methods require a heavy metal catalyst and/or provide very low yields.[8] From these points of view, we report herein on the unique CO_2-induced vicinal aminochlorination of olefins with CT, which expands the utility of the potential nitrogen source in organic synthesis.

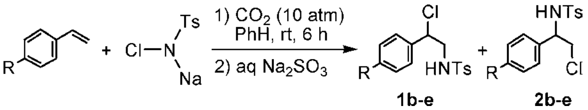
Table 1. Addition of Chloramine-T (CT) to Styrene under CO_2



entry	solvent	atmosphere (atm)	yield (%) 1a	2a
1	MeCN	N_2 (1)	0	0
2	MeCN	CO_2 (1)	1	13
3	MeCN	CO_2 (30)	38	7
4	Et_2O	CO_2 (30)	9	2
5	THF	CO_2 (30)	25	0
6	CH_2Cl_2	CO_2 (30)	54	0
7	PhH	CO_2 (30)	63	0
8	PhH	CO_2 (50)	57	0
9	PhH	CO_2 (20)	78	0
10	PhH	CO_2 (10)	80[a]	0
11	PhH	CO_2 (5)	16	0
12	PhH	N_2 (30)	0	0

[a] Reaction time: 9 h.

Table 2. Addition of CT to Styrene Derivatives under CO_2

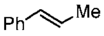
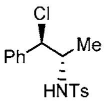
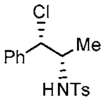
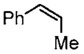
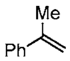
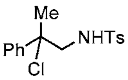
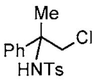
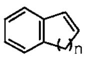
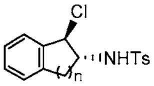
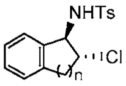
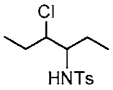
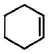
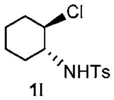
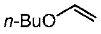
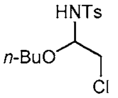


entry	R	yields (%) 1	2
1	NO_2	(**1b**) 71	(**2b**) 0
2	Cl	(**1c**) 74	(**2c**) 0
3	Me	(**1d**) 54	(**2d**) 9
4	MeO	(**1e**) 0	(**2e**) 76

When styrene was treated with CT (1 equiv) under an atmosphere of nitrogen at room temperature for 6 h, no reaction was observed (Table 1, entry 1). The presence of CO_2 permitted the desired aminochlorination to proceed, giving a small amount of **1a** as well as **2a** in 13% yield after treatment with aqueous Na_2SO_3 (Table 1, entry 2). Interestingly, increasing the pressure of CO_2 to 30 atm not only improved the total yield but also reversed the selectivity of these products (Table 1, entry 3), though the drastic change of the regioselectivity could not be explained at present. A reaction was then conducted under 30 atm of CO_2, using a range of solvents, including ether, THF, CH_2Cl_2, and benzene. Among these solvents, benzene was found to be the best solvent to give **1a** as the sole regioisomer in 63% yield (Table 1, entries 4−7). Although the use of 50 atm of CO_2 was not effective for the aminochlorination, decrease of the pressure to 10 atm improved the efficiency of the reaction, affording the desired **1a** in 80% yield (Table 1, entries 8−10). Unfortunately, the lower pressure of CO_2 (5 atm) gave a poor result (Table 1, entry 11). To confirm that the addition reaction did not occur under pressure conditions without contribution of CO_2, the reaction was conducted under 30 atm of N_2 to result in no reaction (Table 1, entry 12).

To investigate the active species of the reaction, *p*-substituted styrenes were subjected to the aminochlorination (Table 2). The addition reaction of CT to *p*-nitro- and

Table 3. Aminochlorination of Olefins with CT under CO_2[a]

entry	olefin	yield (%)	adducts (ratio)	
1		62	 **1f** (84 :	 **1g** 16)
2		81		
3[b]		66	 **1h** (83 :	 **2h** 17)
4 5		70 (n = 1) 68 (n = 2)	 n = 1 **1i** (90 : n = 2 **1j** (78 :	 **2i** 10) **2j** 22)
6		28	 **1k**	
7		27	 **1l**	
8		57	 **1m**	

[a] Reaction conditions: olefin (1 mmol), CT (1 mmol), CO_2 (10 atm), PhH (3 mL), rt, 6 h. [b] At 70 °C.

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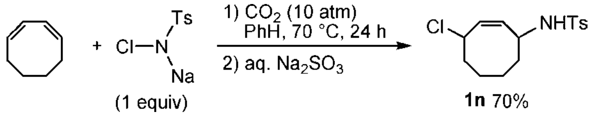
chlorostyrene, in the presence of CO_2, at a pressure of 10 atm, proceeded regioselectively to give **1b** and **1c**, respectively, in good yields (Table 2, entries 1 and 2), with the same selectivity as that observed for styrene, as shown in Table 1. In the aminochlorination of *p*-methylstyrene under the same conditions, two regioisomers **1d** and **2d** were obtained (Table 2, entry 3). *p*-Methoxystyrene was completely transformed to *β*-chlorinated **2e** in 76% yield (Table 2, entry 4). These results indicate that the reaction might proceed through an ionic species.

A variety of olefins were examined for aminochlorination with CT under CO_2 (Table 3). While the aminochlorination of *trans*- and *cis*-*β*-methylstyrene proceeded in good yields and complete regioselectivity, two diastereomers[9] were obtained with *anti*-selectivity in the same ratio, respectively. α-Methylstyrene was also aminochlorinated to afford predominantly the α-chlorinated compound. The aromatic cyclic olefins, indene and 1,2-dihydronaphthalene, were readily converted to the corresponding *anti*-adducts with two regioisomers, where α-chloro derivatives were mainly produced. Aliphatic olefins were found to be applicable to the reaction as well, although the efficiency needs to be improved. An electron-sufficient olefin, butyl vinyl ether, was a good substrate for aminochlorination leading to a regiocontrolled adduct.

To demonstrate the utility of the system, the reaction of a conjugated diene was examined. When 1,3-cyclooctadiene was treated with CT under CO_2 (10 atm) at 70 °C in benzene, a 1,4-adduct was obtained as the sole product[10] in 70% yield without the formation of any 1,2-adduct.

Scheme 1. 1,4-Addition of CT to 1,3-Cyclooctadiene under CO_2



In summary, a new type of aminohalogenation of olefins has been developed using a unique combination of CT and CO_2. The present method could be applied to a variety of olefins, including an electron-sufficient olefin and a conjugated diene. This unprecedented addition is heavy-metal-free, noncatalytic, and is an atom-economical process. The mechanistic consideration[11] and the introduction of CO_2 to organic molecules based on this system is currently underway.

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Supporting Information Available: Experimental details and spectral data for the major products. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] The spectroscopic data of compounds **1f** and **1g** were in agreement with those for the previously reported compounds. See: Flores-Parra, A.; Suárez-Moreno, P.; Sánchez-Ruíz, S. A.; Tlahuextl, M.; Jaen-Gaspar, J.; Tlahuext, H.; Salas-Coronado, R.; Cruz, A.; Nöth, H.; Contreras, R. *Tetrahedron: Asymmetry* **1998**, *9*, 1661−1671.

[10] Although the stereochemistry of the product was not determined, one isomer was obtained.

[11] Since the mechanism of the present reaction is very interesting, the detail should be clarified in near future.