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A Free-Radical Cascade Trifluoromethylation/Cyclization of *N*-Arylmethacrylamides and Enynes with Sodium Trifluoromethanesulfinate and Iodine Pentoxide

Lizhi Zhang, Zejiang Li, and Zhong-Quan Liu*

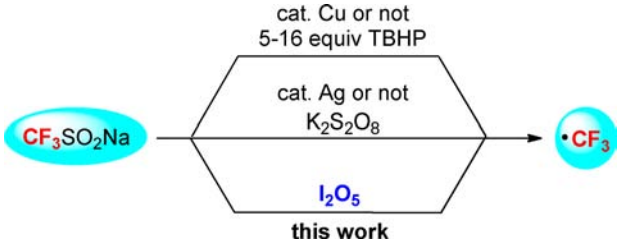
State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou Gansu 730000, P. R. China

Supporting Information

ABSTRACT: An I_2O_5-promoted free-radical cascade trifluoromethylation/cyclization of a broad range of *N*-arylmethacrylamides and enynes with sodium trifluoromethanesulfinate in aqueous medium has been achieved. This strategy allows highly selective access to a variety of CF_3-containing oxindoles and pyrrolidines. Electron spin resonance (ESR) studies indicate that atom-transfer processes are involved in this system.

A wide range of pharmaceuticals and agrochemicals bear a trifluoromethyl (CF_3) group mainly because it can dramatically modify their nature, such as their lipophilicity, electronegativity, metabolic stability, and bioavailability.[1] Therefore, recent advances in exploring more efficient strategies for trifluoromethylation have been made.[2] Recently, significant developments have been achieved by transition-metal-catalyzed/-promoted[3] as well as free-radical-mediated trifluoromethylation.[4] Among the radical systems, several reagents such as CF_3X (X = Br, I), CF_3SO_2X, $TMSCF_3$, Umemoto's reagent [*S*-(trifluoromethyl)dibenzothiophenium tetrafluoroborate], and Togni's reagent (1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one and 1-trifluoromethyl-1,3-dihydro- 3,3-dimethyl-1,2-benziodoxole), etc., have been used as the trifluoromethyl radical sources.[5] In contrast to these reagents, sodium trifluoromethanesulfinate (CF_3SO_2Na, Langlois reagent), a stable and inexpensive solid, has gained much attention only in recent years.[6] In 2011, Baran et al. reported a very efficient trifluoromethylation of heterocycles by using Langlois reagent.[7] Later, several radical methods using CF_3SO_2Na have been developed by Sanford,[8] Maiti,[9] Qing,[10] and us.[11] As depicted in Scheme 1, in the previous trifluoromethylation reactions with Langlois reagent, the strategies for generation of the trifluoromethyl radical can be mainly summarized in two pathways. One is mediated by *tert*-butyl hydroperoxide (TBHP) with or without copper catalyst.[6−8,10,11] The second method is promoted by air or oxygen in the presence of silver salts and $K_2S_2O_8$.[9] However, these systems required large excess amounts of potentially explosive peroxide and/or metal catalyst. Although a very recent example of trifluoromethylation of arenes with CF_3SO_2Na and phenyliodine bis(trifluoroacetate) (PIFA) was reported by Shibata and co-workers, this system was limited in electron-rich arenes.[12] More safe and practical trifluoromethylation strategies are highly desirable.

Scheme 1. Strategies for Generation of Trifluoromethyl Radical from CF_3SO_2Na



With particular interest in free-radical-initiated trifluoromethylation, we began to hypothesize that a nonmetal inorganic single-electron oxidant would promote a CF_3-derivatived anion (e.g., $CF_3SO_2^-$) to generate the trifluoromethyl radical. In our previous studies, we found that some nonmetal inorganic iodines such as iodic acid (HIO_3, IA) and iodine pentoxide (I_2O_5, IP) can be used as reliable and safe single-electron oxidants.[13] Despite their wide applications in chemical industry because of their low price and particular stability,[14] IA and IP are rarely used in organic synthesis.[15] Inspired by these previous investigations on IA/IP-promoted single-electron-transfer (SET) reactions, we reasoned that it could trigger a series of free-radical trifluoromethylations through single-electron oxidation of CF_3SO_2Na. Herein, we report an IP-promoted trifluoromethylation/cyclization of *N*-arylmethacrylamides and enynes with Langlois reagent.

The CF_3 motif is becoming an increasingly common unit among important heterocycles found in agrochemicals and pharmaceuticals, which supplies a driving force for the exploration of more powerful and practical trifluoromethylation protocols.[3j,6b,c,7] Recently, several efficient methods have been developed to construct trifluoromethylated oxindoles and pyrrolidines by using Togni's reagent with or without transition-metal catalysis.[3m−o,u] In order to realize a safe, low-

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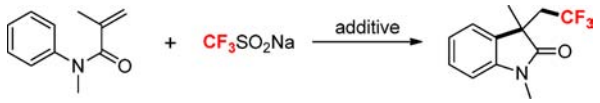
Table 1. Modification of the Typical Reaction Conditions[a]



entry	oxidant (equiv)	solvent (v/v, V)	temp (°C)	yield[b] (%)
1		CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	50	
2[c]	IP (3)	CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	50	**76**
3	IP (3)	CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	50	**84**
4	IA (6)	CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	50	**51**
5	PIFA (3)	CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	50	**37**
6	IBX (3)	CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	50	
7	IP (3)	H_2O (3.5 mL)	50	6
8	IP (3)	DMSO/H_2O (2.5/1, 3.5 mL)	50	31
9	IP (3)	CH_2Cl_2/H_2O (1/1, 3.5 mL)	50	52
10	IP (3)	CH_2Cl_2/H_2O (2.5/1, 3.5 mL)	25	5
11	**IP (3)**	**CH_2Cl_2/H_2O (2.5/1, 3.5 mL)**	**70**	**89**
12	IP (3)	CH_2Cl_2/H_2O (2.5/1, 2 mL)	70	12
13	IP (3)	CH_2Cl_2/H_2O (2.5/1, 5 mL)	70	26
14	IP (3)	CH_2Cl_2/H_2O (2.5/1, 10 mL)	70	5

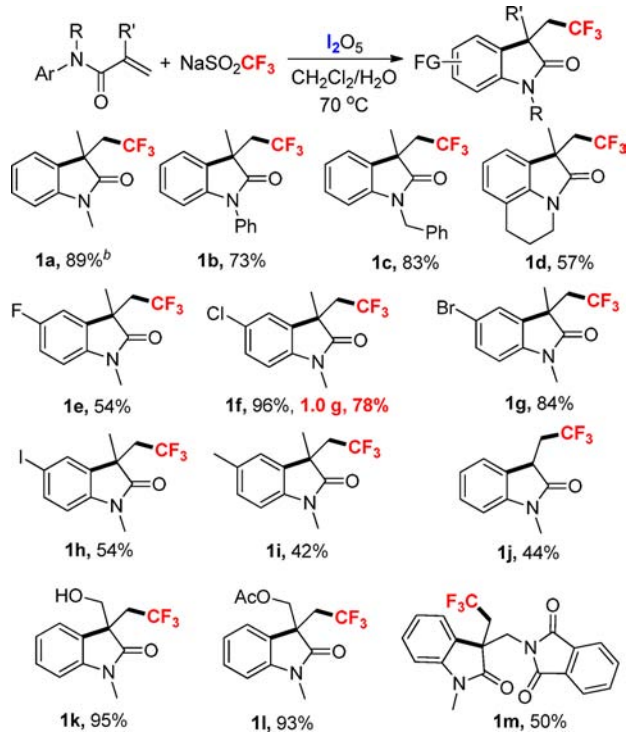
[a]Reaction conditions: *N*-methyl-*N*-phenylmethacrylamide (1 equiv, 0.2 mmol), $NaSO_2CF_3$ (5 equiv, 1.0 mmol), 22 h, sealed tube. [b]Isolated yields. [c]$NaSO_2CF_3$ (3 equiv, 0.6 mmol).

cost, and practical strategy for introduction of CF_3 into heterocycles, we chose *N*-methyl-*N*-phenylmethacrylamide and sodium trifluoromethanesulfinate as the model substrates to optimize the suitable conditions for this transformation (Table 1 and the Supporting Information). It was found that the oxidants and solvent critically affect the efficiency of the reaction. No product was observed without oxidant (Table 1, entry 1). It was found that several organic hypervalent iodines such as $PhI(OCOCF_3)_2$ and 2-iodoxybenzoic acid (IBX) as well as HIO_3 were much less efficient than IP (Table 1, entries 2–6). We found that a mixed solvent of CH_2Cl_2/H_2O with a ratio of 2.5/1 was better than others such as H_2O, DMSO/H_2O, etc. (Table 1, entries 7–9). When the reaction was conducted at 25 and 70 °C, the desired product was isolated in 5% and 89% yield, respectively (Table 1, entries 10 and 11). Finally, the cage effect of this reaction was also investigated (Table 1, entries 12–14). As a result, higher or lower concentrations of the alkene (compared to 0.057 mol/L) all led to much lower yields of the product.

As depicted in Scheme 2, trifluoromethylated oxindole and its derivatives were isolated in moderate to nearly quantitative yields under the typical reaction conditions (**1a–m**). The *N*-methyl-, *N*-phenyl-, *N*-benzyl-, and *N*-alkyl-substituted *N*-phenylmethacrylamides all gave the desired products in good to high yields (**1a–d**). Gratifyingly, the amides with halogen atoms such as F, Cl, Br, and I as well as alkyl substituents on the *para*-position of the *N*-aryl moiety led to moderate to nearly quantitative yields of the corresponding products (**1e–i**). It is noteworthy that the reaction can be scaled-up to gram level without losing efficiency (**1f**, 1.0 g, 35 h, 78% yield). The *N*-methyl-*N*-phenylacrylamide gave the CF_3 bearing oxindole in 44% yield (**1j**). In addition, functional groups such as hydroxyl, ester, and amine at the 2 position of the acrylamide core could be well tolerated in this system (**1k–m**).

To apply this strategy in other systems, we studied the trifluoromethylation/cyclization of enynes with IP/$NaSO_2CF_3$. An efficient and highly selective trifluoromethylation–cyclization–iodination of an array of enynes is also achieved via a single step under conditions similar to those of the former

Scheme 2. I_2O_5-Mediated Trifluoromethylation/Cyclization of *N*-arylmethacrylamides[a]



[a]Reaction conditions: *N*-arylmethacrylamides (1 equiv, 0.2 mmol), $NaSO_2CF_3$ (5 equiv, 1.0 mmol), I_2O_5 (3 equiv, 0.6 mmol), CH_2Cl_2/H_2O (2.5/1, 3.5 mL), 70 °C, 22 h, sealed tube. [b]Isolated yields.

reaction (Scheme 3). As illustrated in Scheme 3, the trifluoromethylated five-membered *N*-heterocycles were obtained with specific regioselectivity, which indicated that the 5-*exo-dig* cyclization represented the exclusive pathway (**2a–g**). It was found that there was no evident electronic effect since various enynes containing aromatic cores with both electron-donating and electron-withdrawing groups resulted in moderate to high yields of the desired products (**2a–f**). In the case of

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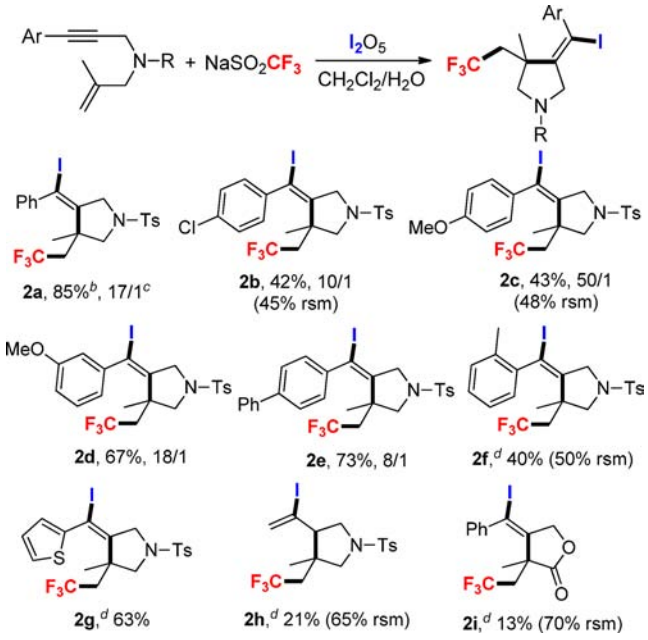
Scheme 3. I_2O_5-Mediated Trifluoromethylation/Cyclization of Enynes[a]

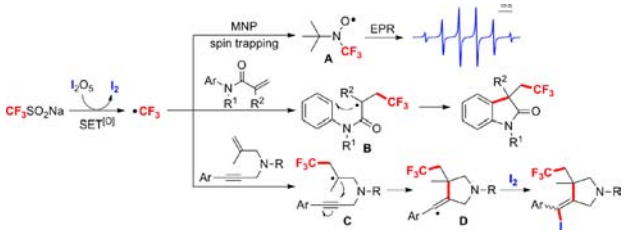


[a]Reaction conditions: enyne (1 equiv, 0.2 mmol), $NaSO_2CF_3$ (3 equiv, 0.6 mmol), I_2O_5 (3 equiv, 0.6 mmol), CH_2Cl_2/H_2O (2.5/1, 3.5 mL), 110 °C, 20 h, sealed tube. [b]Isolated yields. [c]Ratio of the *E*/*Z* isomers determined by ^{19}F NMR spectroscopy. [d]Only one isomer was observed.

enynes bearing aryls with either *meta*- or *ortho*-substituents, moderate to good yields of the pyrrolidines were obtained, which suggests the steric effect is not obvious (**2d** and **2f**). It is noteworthy that thiophene-substituted enyne can also act as an effective substrate in this system (**2g**). Interestingly, *N*-(buta-2,3-dien-1-yl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide gave the corresponding **2h** as the major product, suggesting the allene group can be tolerated. Finally, 3-phenylprop-2-yn-1-yl methacrylate also led to the desired product **2i**, although the yield was low. The features of step economy, functional group tolerance, and high selectivity make this method very attractive.

To gain insight into the details of the mechanism, we carried out a series of mechanistic studies through spin-trapping technology and electron-spin resonance (ESR) (Scheme 4). When 2-methyl-2-nitrosopropane (MNP) was used as a radical spin trap, the signals of the radical adduct trifluoromethyl *tert*-butyl nitroxide radical **A** were clearly recorded by ESR. the relatively stable nitroxide radical **A** would be formed by addition of CF_3 radical to MNP. The *g* value (2.0061) and the hyperfine coupling constant ($a_N = a_F = 12.25$ G) obtained in this system are consistent with the reported data.[16] In the case of *N*-arylmethacrylamide, addition of the CF_3 radical to the double bond would generate radical **B**, which then adds to the aromatic core followed by aromatization forming the trifluoromethylated oxindole. Similarly, the trifluoromethyl radical adds to the C=C double bond of enyne leading to a β-CF_3-alkyl radical intermediates **C**, which occurs a free-radical 5-*exo*-*dig* cyclization to give an alkenyl radical **D**. The product is formed via capture of iodine by radical **D**. We proposed that the I_2 might come from I_2O_5 through multistep redox processes. The formation of I_2 has also been confirmed by observation of an obvious color change while starch was added into the system though the mechanistic details of the redox processes are not very clear at the presence. Overall, a free-radical cascade cyclization pathway would be involved in both of the trifluoromethylation reactions.

Scheme 4. Proposed Mechanism and Spin Trapping of the Radical Intermediates



In conclusion, an I_2O_5-promoted highly selective and scalable trifluoromethylation/cyclization cascade reaction of *N*-arylmethacrylamides and enynes with $NaSO_2CF_3$ in aqueous medium has been developed. A wide range of trifluoromethylated oxindoles and pyrrolidines are efficiently prepared by using this strategy. EPR studies indicate that free radical processes would be involved in this system. Further studies on the IP-promoted SET reactions are ongoing in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details and characterization data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: liuzhq@lzu.edu.cn.

Notes

The authors declare no competing financial interest.

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