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Rhenium-Catalyzed Trifluoromethylation of Arenes and Heteroarenes by Hypervalent Iodine Reagents

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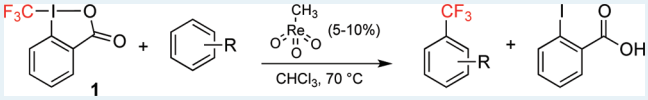
Supporting Information

ABSTRACT: Methyltrioxorhenium acts as a catalyst (5−10 mol %) for the direct electrophilic trifluoromethylation of various aromatic and heteroaromatic compounds using the hypervalent iodine reagent 1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one (**1**). The products are formed in up to 77% yield. Mixtures of regioisomers are obtained in the case of substituted and heteroaromatic substrates. The reaction, typically carried out in chloroform solvent at 70 °C, shows a significant induction period. Monitoring by EPR shows the involvement of radical species. A small kinetic deuterium isotope effect of 1.3 is observed for benzene.



KEYWORDS: *methyltrioxorhenium, electrophilic trifluoromethylation, catalytic trifluoromethylation, hypervalent iodine, radical reactions*

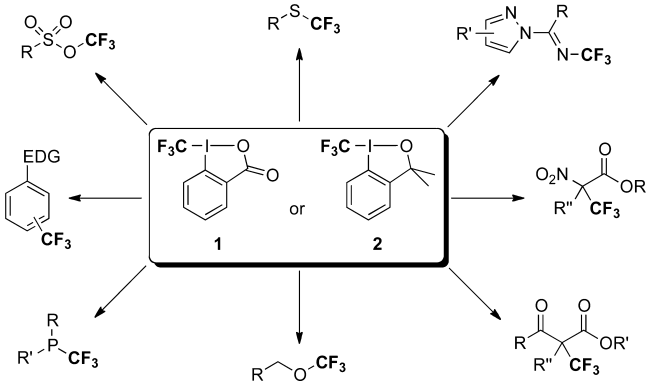
INTRODUCTION

In recent years, organofluorine compounds have played a major role not only in the pharmaceutical industry, with hundreds of F-containing drugs on the market,[1] but also in the agrochemical industry and in materials science. Among the plethora of fluorinated organic compounds available, those containing a perfluoroalkyl group deserve special attention because of their high stability and remarkable solubility properties.[2] However, amenable methods for the introduction of fluorine or perfluoroalkyl groups into organic compounds are still scarce and are the object of high current research efforts. Among those, direct trifluoromethylation, either radical, nucleophilic, or electrophilic, is one of the most powerful and straightforward methodologies.[3−6]

Introduction of the CF_3 moiety into aromatic and heteroaromatic compounds is not a trivial task. It has been typically carried out by radical trifluoromethylation using, for example, $(CF_3)_2E$ (E = Te, Hg);[7] Umemoto's TNS-Tf (*N*-trifluoromethyl-*N*-nitrosotrifluoromethanesulfonamide);[8] bis(trifluoroacetyl) peroxide;[9] trifluoroacetic acid in the presence of XeF_2;[10] or more recently, CF_3I in the presence of Fe(II) compounds,[11] albeit giving only moderate yields. One way to circumvent this problem is the copper-mediated substitution of functionalized aromatic substrates (i.e., iodides[12−17] or boronic acids[18−20]), which require stoichiometric amounts of metal, or the more elegant palladium-catalyzed version, which gives excellent results with less than 0.1 equiv of catalyst.[21−23] The main drawback in the cases mentioned above is that a corresponding prefunctionalized precursor is required. Thus, a simple method for the direct trifluoromethylation of nonfunctionalized arenes (and heteroarenes) under mild conditions is desirable.

In 2006, our group developed a new class of electrophilic trifluoromethylating reagents based on hypervalent iodine, including 1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one (**1**) and trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (**2**),[24,25] both easily accessible in high yields from *o*-iodobenzoic acid, and commercially available CF_3TMS (Ruppert−Prakash reagent).[26,27] Reagents **1** and **2** have been used successfully in our laboratories for the direct electrophilic trifluoromethylation of *β*-keto esters,[24] sulfur centered nucleophiles,[28] *α*-nitro esters,[28] phosphines,[29] phenolates,[30] and alcohols[31] and for the Ritter-type N-trifluoromethylation of nitriles[32] (Scheme 1).

Scheme 1. Some Applications of Hypervalent Iodine Trifluoromethylation Reagents 1 and 2



Finally, several other research groups have used reagents **1** or **2** for the trifluoromethylation of a variety of substrates.[33−38]

Recently, we also reported the trifluoromethylation of *N*-heteroarenes and activated arenes under mild conditions. These transformations commonly require the use of substoichiometric

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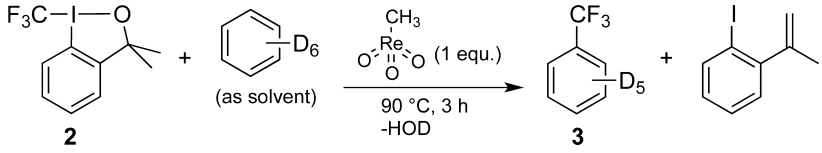
Scheme 2. Trifluoromethylation of Benzene by Reagent 2 in the Presence of MTO



amounts of tris(trimethylsilyl)silyl chloride or a zinc salt as additives.[39] Furthermore, similar reactions focusing on the trifluoromethylation of indole derivates and hetero arenes have been reported more recently by other research groups.[40−42] Newest examples of direct trifluoromethylations of arenes and heterocycles have involved an iridium-catalyzed borylation combined with a consecutive Cu-assisted introduction of the CF_3 group,[43,44] the use of $TMSCF_3$ in the presence of a large excess of a silver salt,[45] and the reaction of highly substituted heterocycles with sodium trifluoromethanesulfinate in the presence of an oxidant.[46]

RESULTS AND DISCUSSION

In an attempt to prepare a trifluoromethylated derivative of methyltrioxorhenium (MTO)[47] using reagent **2** in benzene-d_6, we surprisingly observed the formation of deuterated benzotrifluoride (**3**) as the main trifluoromethylated product (Scheme 2).

Further experiments showed that reagent **1** effected this transformation even faster and in higher yields of **3**. Therefore, we chose it along with benzene-d_6 as substrate to optimize the reaction conditions (Scheme 3, Table 1). It is important to note that the reaction with either reagent **1** or **2** does not proceed in the absence of the rhenium catalyst, showing only in some cases trace amounts of product. The reactions were conducted overnight to guarantee full conversion, although they were usually complete after ∼2 h, as indicated by the darkening of the reaction mixture. The main side product of the reaction is the trifluoromethyl ester of *o*-iodobenzoic acid (**4**) which corresponds to the decomposition product of **1** in the presence of either Lewis or Brønsted acids, as reported previously.[48]

Scheme 3. Model Reaction Used for the Optimization of Conditions for the Trifluoromethylation of Benzene by Reagent 1 with a Re Catalyst

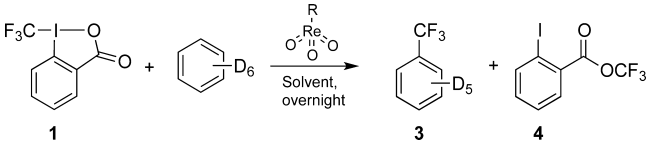


Table 1. Screening of Reaction Conditions for the Trifluoromethylation of Benzene-d_6 with Reagent 1

entry[a]	solv.	T (°C)	C_6D_6 (equiv)	1 (equiv)	cat. (equiv)	3[b] (%)	3:4[b]
1	CD_2Cl_2	70	1	1	0.08	41	14:1
2	CD_2Cl_2	70	1.5	1	0.09	53	18:1
3	CD_2Cl_2	70	3	1	0.08	54	11:1
4	CD_2Cl_2	70	1	1.5	0.09	48	7:1
5	CD_2Cl_2	40	1.5	1	0.08	trace	-
6	CD_2Cl_2	70	1.5	1	0.24	47	16:1
7	$CDCl_3$	70	1.5	1	0.08	54	108:1
8	$CDCl_3$	70	1.5	1	0.02	51	17:1
9	$CDCl_3$	70	1.5	1	0.01	31	4:1
10[c]	$CDCl_3$	70	1.5	1	0.07	44	11:1

[a]Reaction conditions: limiting reagent (1 equiv) ∼0.1 M in a closed Young-type NMR tube; R = methyl. [b]Calculated by ^{19}F NMR using perfluoronaphthalene as internal standard. [c]R = mesityl.

In most cases, CF_3I, CF_3H and CF_3D were formed as the main byproduct, although the exact amounts were not determined due to the volatility of these compounds. It was observed that better results were achieved when a slight excess of substrate was used. The optimal catalyst loading was between 5 and 10%. The solvent of choice was chloroform in which decomposition of **1** to **4** was minimized to less than 1% (Table 1, entry 7). A second rhenium complex, namely, mesityltrioxorhenium,[49] was also shown to be active, but to a lower extent (Table 1, entry 10).

Once the best reaction conditions were established (Table 1, entry 7), we examined the trifluoromethylation of several arenes bearing different functional groups (Table 2). The reaction proceeded in all cases, giving higher yields with aromatic compounds bearing electron-donating groups. The best results were obtained for anisol derivates (Table 2, entries 4 to 7). Contrary to what has been reported previously from our laboratory,[39] the electrophilic trifluoromethylation of non-activated or electron-poor aromatic systems was possible, although in moderate yields (Table 2, entries 10−15). Under the reaction conditions mentioned above, we were also able to achieve the first direct trifluoromethylation of ferrocene (Table 2, entry 16). It is also worth mentioning that traces of the bistrifluoromethylated product were observed by GC/MS analysis in several cases (see Supporting Information).

The scope of the reaction was further extended to oxygen-, sulfur-, and nitrogen-containing heteroaromatic substrates (Table 3). The highly electron-rich 1-benzofuran and 1-benzothiophene showed moderate yields, probably due to strong coordination of the substrate to the catalyst. Better results were obtained for 1*H*-indole and its derivatives (Table 3, entries 3−5), and in the case of 3-methylindole, the regioselective trifluoromethylation at the more electron-rich 2 position afforded 75% yield. In addition, pyridines were successfully trifluoromethylated under these conditions, albeit with modest yields when electron-withdrawing or bulky substituents were present (Table 3, entries 6−18). The introduction of methoxy groups showed two competing effects: electron-enrichment that, as seen before, favors the electrophilic trifluoromethylation and an increase in the basicity of the substrate,[50,51] which could lead to decomposition of the catalyst (Table 3, entries 15−18).

To obtain possible insights into the reaction mechanism, we monitored the trifluoromethylation of benzene-d_6 (1.5 equiv, ∼0.1 M) in $CDCl_3$ with 1 equiv of reagent **1** in the presence of a catalytic amount of MTO (0.08 equiv) at 70 °C for 3 h by ^{19}F NMR spectroscopy (Figure 1).

The observed time vs yield profiles show a significant induction period of 1 h, after which the reaction goes to completion within 20 min. The corresponding sigmoid curves suggest a mechanism possibly involving autocatalysis or radical processes.

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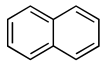
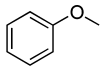
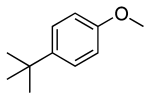
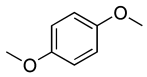
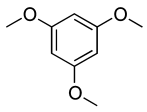
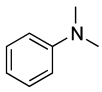
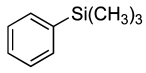
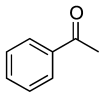
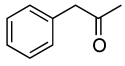
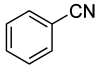
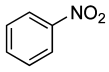
Table 2. Trifluoromethylation of Arenes Using Reagent 1 and MTO as Catalyst

Entry[a]	Substrate	Total yield (%)[b]	Isomer ratio[b]		
			o-	*m*-	*p*-
1		54	-	-	-
2		58	1.3	1	2.4
3		58	5.4 (α)	1 (β)	-
4		62	2.6	1	1.3
5		63	1	n.d.	-
6		70	-	-	-
7		77	-	-	-
8		49	5.5	1	9.1
9		45	n.d.	n.d	n.d
10		42	1.6	1	1.1
11		41	1.3	1	1
12		32	1.3	1	1.9
13		31	1	1	1
14		~15	1	n.d.	1
15		13	1	3.5	10
16		33	-	-	-

[a]Reaction conditions: reagent **1** (1 equiv) ~0.1 M in $CDCl_3$ in a closed Young-type NMR tube; 1.5 equiv of substrate; 70 °C, overnight; MTO (5−8%) used as catalyst; n.d. = not determined. [b]Calculated by ^{19}F NMR using perfluoronaphthalene as internal standard.

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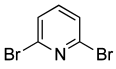
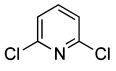
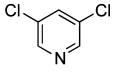
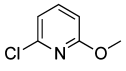
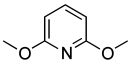
Table 3. Trifluoromethylation of Heteroarenes Using Reagent 1 and MTO as Catalyst

Entry[a]	Substrate	Total yield (%)[b]	Isomer ratio[b] 2-	3-	7- or 4-
1[c]		43	2.4	1	-
2		45	1.1	1	1
3		59	3.4	1	1.5
4[d]		64	2.8	1.2	1
5		75	1	-	n.d.
6		38	4.3	3.0	1
7		~25	-	n.d.	1
8[d]		50	n.d.	n.d.	n.d.
9[e]		20	1	n.d.	-
10[d]		36	1(6-)	1.5(5-)	2.8(3-)
11[f]		24	1	n.d.	-
12		11	-	n.d.	1
13		14	-	n.d.	1
14[g]		18	1	-	n.d.
15		48	-	1	3.3(5-)
16		60	-	13	1
17		33	1(6-)	1.6(5-)	7(3-)
18		Trace	n.d.	n.d.	-

[a]Reaction conditions: reagent **1** (1 equiv) ~0.1 M in $CDCl_3$ in a closed Young-type NMR tube; 1.5 equiv of substrate; 70 °C, overnight; MTO (5–8%) used as catalyst; n.d. = not determined. [b]Calculated by ^{19}F NMR using perfluoronaphthalene as internal standard. [c]23% of CF_3H formed. [d]36–39 h. [e]~300 h. [f]95 h. [g]24 h.

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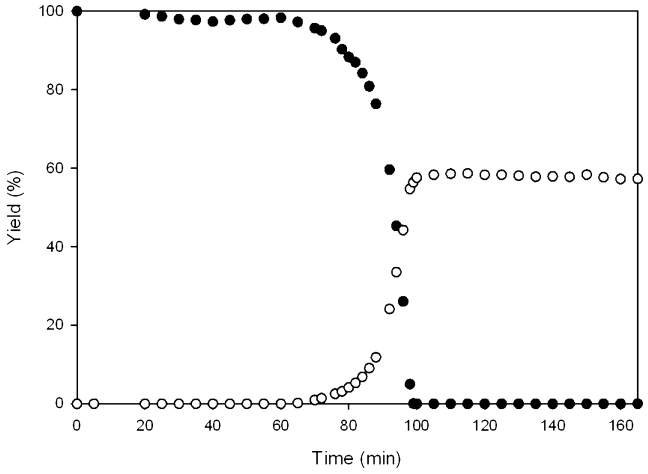

Figure 1. Reaction profile for the trifluoromethylation of benzene-d_6 as monitored by ^{19}F NMR, showing the consumption of **1** (solid circles) and the formation of benzotrifluoride (open circles). Reaction conditions: reagent **1** ~0.1 M in $CDCl_3$; 1.5 equiv of substrate; 0.08 equiv of MTO; 70 °C. Perfluoronaphthalene was used as internal standard.

Therefore, to check the involvement of radical species in the reaction, EPR monitoring of the reaction was carried out. To this end, we selected 4-*t*-butylanisol as substrate because of the relatively high stability of its radicals, which would lead to a facile detection.[52] The reaction profile showed (as in the case of benzene by NMR) an induction period of ~1 h, after which the concentration of radical species rises suddenly and is consumed within ~30 min (Figure 2), which is in full agreement with the

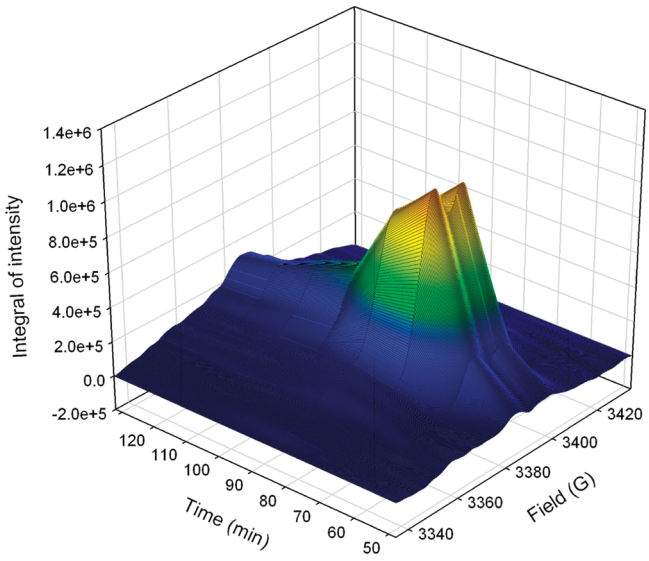

Figure 2. Reaction profile for the trifluoromethylation of 4-*t*-butylanisol as monitored by EPR. Reaction conditions: reagent **1**, 0.17 M in $CDCl_3$; 3.3 equiv of substrate; 0.86 equiv of MTO; 70 °C.

NMR observations. It is noteworthy that the shape of the EPR signal also changes during the reaction, having at the beginning a pseudodoublet that rapidly collapses into a singlet, meaning that the composition of the radical mixture is not the same.

Deuterium kinetic isotope effect for the re-catalyzed trifluoromethylation with **1** was evaluated by a direct competition reaction between equimolar amounts of benzene and benzene-d_6 used as solvent mixture (for details, see the Supporting Information). After completion, the relative amounts of benzotrifluoride and its deuterated analogue were determined by integration of the signals in the ^{19}F NMR spectrum. Thus, the obtained ratio k_H/k_D = 1.3 represents a small KIE. In general, such a value is typical for a secondary KIE, but less so for a primary KIE. It is therefore not unambiguous to argue for the C−H bond breaking process as constituting the rate-determining step.

Taking these observations and our previous kinetic studies on these kinds of reactions into account,[49,53] we propose the radical chain mechanism depicted in Scheme 4.

The first stage of the reaction, or initiation step (Scheme 4, A), starts with the activation of **1** by coordination to the Lewis acid (MTO),[40,48] making the hypervalent iodine reagent more electrophilic (hence a better oxidant) and thus promoting the single electron transfer from the benzene molecule in the encounter complex **6**.[54,55] This generates an aromatic cation radical species antiferromagnetically coupled with the reduced reagent **1** (singlet diradical **7**).[30] This caged pair would then react via ion-pair collapse[56] with an effective transfer of a CF_3^- moiety to give the radical intermediate **8**. The propagation step (Scheme 4, B) starts with the slow deprotonation of species **8**, probably by **1**, leading to the reactive intermediate **9**, which is rapidly consumed by transfer of a $CF_3^\bullet$ unit to the substrate, closing the cycle. The termination step would be the decomposition of **8** (after consumption of **1**), leading to CF_3H and CF_3D, formed only in the latest stage of the reaction, as observed by NMR (see Supporting Information.)

CONCLUSION

We disclosed a potential novel methodology for the direct trifluoromethylation of both activated and inactivated arenes and heteroarenes using an easily accessible, shelf-stable, hypervalent iodine trifluoromethylating reagent (**1**) and MTO as catalyst. Only a small excess of substrate and 5−10% of catalyst are required. To the best of our knowledge, this is the direct aromatic trifluoromethylation reaction with the broadest substrate scope so far, despite the low yields obtained in the case of substrates bearing electron-withdrawing substituents. We are currently engaged in more detailed studies of this reaction with the aim of clarifying mechanistic aspects, broadening its scope, and turning it into a synthetically applicable procedure.

EXPERIMENTAL SECTION

General procedure for the trifluoromethylation of arenes and heteroarenes: A dried Young-type NMR tube was charged with 1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one (**1**, 12.6 mg, 0.04 mmol), 100 μL of a stock solution of perfluoronaphthalene in $CDCl_3$ containing 0.01 mmol (used as internal standard), and 100 μL of a freshly prepared stock solution of methyltrioxorhenium (MTO) in $CDCl_3$ containing 0.08 equiv (0.003 mmol). To the colorless solution, 1.5 equiv (0.06 mmol) of the aromatic substrate and $CDCl_3$ was added to afford a final volume of 0.5 mL. The mixture was heated at 70 °C until the color changed to dark brown. The mixture was allowed to cool to room temperature, and after the corresponding NMR analysis, it was filtered through a plug of alumina-N eluting with acetone. The resulting colorless filtrate was then subjected to characterization by GC/MS. Further reaction details and characterization of the products is available in the Supporting Information.

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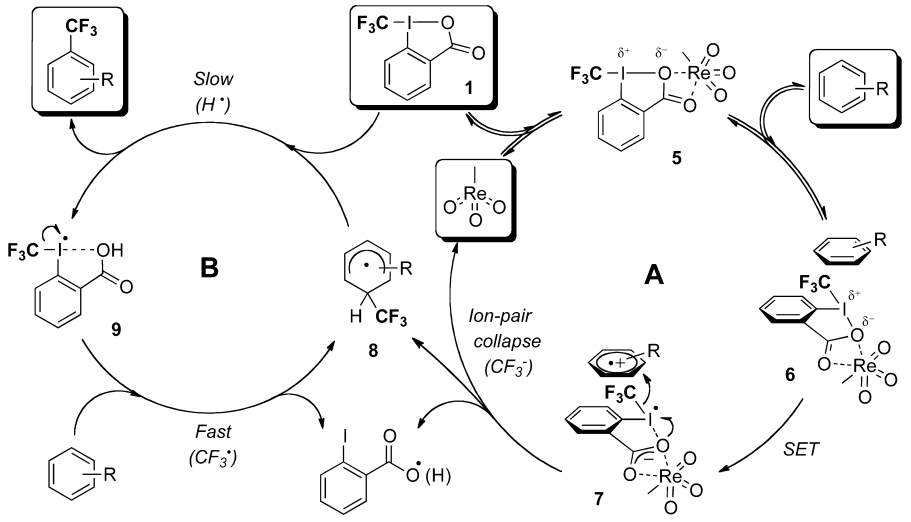
Scheme 4. Proposed Reaction Mechanism for the Rhenium-Catalyzed Trifluoromethylation of Arenes with Reagent 1



■ ASSOCIATED CONTENT

Supporting Information

Characterization of trifluoromethylated products, details of ^{19}F NMR and EPR monitoring experiments, Copies of ^{19}F NMR and GC-MS spectra of reaction mixtures. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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