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Ethers as Hydrogen Sources in BF$_3$·OEt$_2$ Promoted Reduction of Diphenylmethyl Alcohols, Ethers and Esters to Hydrocarbons†

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A novel ether/BF$_3$ reductive system has been described, in which diphenylmethanols and their ether and ester derivatives are used as starting materials. Reductions are performed in ether under reflux and argon atmosphere, and an addition of extra water is beneficial to this reduction. A series of alkanes are able to be prepared with good to excellent yields. A deuterated experiment exhibits that the reductive hydrogen is generated from ether. The mechanism is discussed in detail to explain the observed reactivity.

The reduction of carbon-oxygen bonds to the corresponding carbon-hydrogen bonds plays a fundamental role in organic chemistry.[1,2] It is also widely applied in total synthesis chemistry, in which the C-H frame of natural products are constructed with high efficiency.[3] Barton-McCombie deoxygenation is one of the most classic meth-ods, and is well applied by transforming alcohols to their corresponding thiocarbonyl intermediates which undergo radical fragmentation.[4] After Barton-McCombie deoxygenation, several alternative catalytic protocols have been developed employing metal hydrides such as organotin hydride.[5,6] In these strategies, a two-step procedure firstly converts alcohols into preactivated intermediates such as thionocarbonates that are capable of being cleaved readily in reductive steps.[7] Subsequently, the application of a two-step pro-cedure is preferred in the deoxygenation of alcohol derivatives such as aryl sulfonates (e.g. triflates, tosylates, mesylates), arylthiocarbonates, ethers and esters mediated by Pd-,[8] Ni-[9a-c] and Rh-based catalysts.[9d] In the past decades, many direct dehydroxylation reactions have been reported as well.[10,11] Among these established methods, the combination of hydride reagents with Lewis acids such as LiAlH$_4$/AlCl$_3$,[11a] LiAlH$_4$/TiCl$_3$,[11b] and NaBH$_4$/AlCl$_3$[11c] seems to increase the reactivity of hydride. Dehydroxylations of primary, secondary, and tertiary alcohols have been developed by employing

hydrosilanes/metallic Lewis acids systems such as Ph$_2$SiHCl/InCl$_3$,[12a] Et$_3$SiH/PdCl$_2$[12b] and PMHS/PdCl$_2$.[12c] Reduction processes in the presence of nonmetallic Lewis acid B(C$_6$F$_5$)$_3$ are also reported.[13]

BF$_3$·OEt$_2$, generated from the donor-acceptor action between BF$_3$ and Et$_2$O,[14] has shown high activity in many synthetic procedures like alkylation,[15a-d] cyclization,[15e] rearrangement[15f] and coupling reactions.[15g] It was also utilized in the reduction of alcohols,[16a-b] carbonyl compounds[16c] and epoxides[16d] via hydride transfer from hydrosilanes. Our studies have demonstrated that the superacid BF$_3$-H$_2$O promoted benzylation reaction via a carbonium intermediate.[17] We found that when iodobenzene was involved as both arene and solvent, the benzylation product was not produced and the undesired diphenylmethane was obtained in 47% yield by a reductive mechanism. The source of hydrogen was thought to come from the diphenylmethanol or diethyl ether by disproportionation, accompanied with the generation of reductive hydrogen. However, no diphenylketone was detected, which indicated that hydrogen was released very probably from the selfoxidation of ether ligand of BF$_3$·OEt$_2$. To test this theory, control experiments were performed in which diphenylmethanol and BF$_3$·OEt$_2$ in dichloromethane led to a 22% yield (see supporting information) and the later deuterated experiment resulted in the D-labelled methene.

The studies on triphenylmethyl cation, in the stable form of trityl salt, can date back to one century ago.[18] Due to its importance in polymer of ether, it was regarded as an excellent initiator of polymerization and kinetically studied extensively covering the hydride ion transfer between triphenylcarbonium and ether. However, for this H transfer, there is no report on relatively unstable diphenylcarbonium ion, due to the unavailability of the salt. Herein, we would like to report our work in BF$_3$·OEt$_2$-promoted reductive reaction of diphenylcarbonium, using diphenylmethanols as well as their ether and ester derivatives as substrates, to corresponding alkanes, employing various ethers as hydrogen sources (Scheme 1).
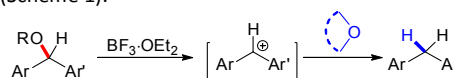
Scheme 1 Proposal in this Work.

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Considering the hydrogen generated from the ether, we chose initially tetrahydrofuran (THF) as a solvent for the reduction of diphenylmethanol (**1a**), and as a result the yield was improved by up to 53% (Table 1, entry 1). As mentioned before,[17] mixing $BF_3 \cdot OEt_2$ with H_2O resulted in the formation of BF_3-H_2O which has shown elevated reactivity in the benzylation of arenes. We assessed the influence of different amounts of H_2O in $BF_3 \cdot OEt_2$ promotion. 0.48 Equivalent of water gave the best results while lower or higher amount of water turned out to be detrimental to this reduction (Table 1, entries 2-4). Then, the treatment of di-phenylmethanol with catalytic amounts (20 mol%) of $BF_3 \cdot OEt_2$ gave rise to diphenylmethane **2a** in 20% yield (Table 1, entry 5). Increasing the amount of $BF_3 \cdot OEt_2$ from 0.6 to 0.8 equivalent resulted in a large improvement of the yield up to 61% (Table 1, entries 6-7). 1.0 Equivalent of $BF_3 \cdot OEt_2$ furnished the desired product in 63% yield with the same level of reactivity compared to 1.2 equivalents of $BF_3 \cdot OEt_2$ (Table 1, entry 8 *vs* 3). However, a lower yield was observed when further increasing the amount of $BF_3 \cdot OEt_2$ (Table 1, entry 9). A solvent screening with diethyl ether, and 2-methyl tetrahydrofuran was conducted and gave moderate yields (Table 1, entries 10-11). When methyl tert-butyl ether (MTBE) and isopropyl ether were utilized as solvent, the reactions went complex and the attempt to separate the product failed (Table 1, entries 12-13). To our delight, employing butyl ether as solvent exhibited excellent reactivity (Table 1, entry 14). Variations of the temperature from 100 ^{o}C to 160 ^{o}C were tested, in which an excellent yield of 87% was obtained under 160 ^{o}C (Table 1, entries 15-17). The optimal reaction conditions were established: 1.0 mmol diphenylmethanol, 1.2 equivalents of $BF_3 \cdot OEt_2$ in 1 mL of butyl ether in argon atmosphere under reflux for 2 h.

Table 1 Optimization of reaction conditions[a]

| Entry	$BF_3 \cdot OEt_2$ (eq.)	H_2O (eq.)	Solvent	Yield (%)[b]
1	1.2	-	THF	53
2	1.2	0.36	THF	55
3	1.2	0.48	THF	62
4	1.2	0.60	THF	52
5	0.2	0.48	THF	20
6	0.6	0.48	THF	52
7	0.8	0.48	THF	61
8	1.0	0.48	THF	63
9	1.5	0.48	THF	52
10	1.2	0.48	Et_2O	53
11	1.2	0.48	2-Methyl THF	55
12	1.2	0.48	MTBE	-[c]
13	1.2	0.48	Isopropyl ether	-[c]
14	1.2	0.48	Butyl ether	83
15	1.2	0.48	Butyl ether	80[d]
16	1.2	0.48	Butyl ether	84[e]
17	1.2	0.48	Butyl ether	87[f]

[a] Conditions: **1a** (1.0 mmol), $BF_3 \cdot OEt_2$ (specified), H_2O (specified) in solvent (1.0 mL) under argon and reflux (oil bath of 120 ^{o}C) for 2 h. [b] Isolated yields. [c] Complex reaction. [d] Oil bath of 100 ^{o}C. [e] Oil bath of 140 ^{o}C. [f] Oil bath of 160 ^{o}C.

Table 2 Substrate scope for diphenylmethanols[a]
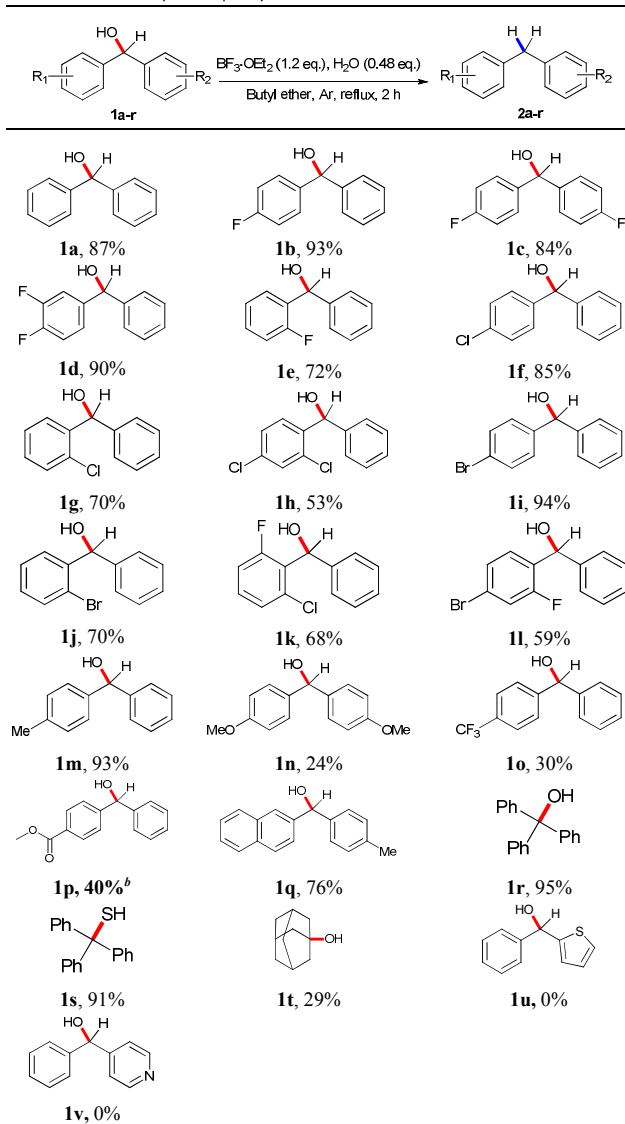
[a] Conditions: **1** (1.0 mmol), $BF_3 \cdot OEt_2$ (1.2 mmol), H_2O (0.48 mmol), oil bath of 160 ^{o}C, butyl ether (1.0 mL) under argon for 2 h. Isolated yields. [b] THF as solvent. oil bath of 120 ^{o}C.

With the optimal reaction conditions in hand, diverse substituted diphenylmethanols bearing mono-/*di*-halo, methyl, and methoxyl groups were investigated with moderate to excellent yields. Considering the potential utilization of fluorine-containing compounds in pharmaceuticals and functionalized materials,[19] fluoro-substituted diphenylmenthanols were chosen as substrates such as 4-fluoro- (**1b**), 4, 4'-difluoro- (**1c**), 3,4-difluoro- (**1d**) and 2-fluoro- (**1e**) substituents. As a result, the corresponding alkanes were obtained in yields of 72-93%. The ortho-fluoro substituent (**1e**) gave a relatively lower yield of 72% than the para-fluoro substitution, probably due to a large extend to the significant steric effects. The chloro- and bromo- substituted aromatics are capable of being further functionalized by $S_N Ar$ reactions, Grignard reactions and coupling reactions, etc. Structurally diverse chloro- and bromo-substituents (**1f-j**) were chosen as substrates, and the yields of 53-

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94% were obtained. It is worthwhile noting that ortho-substitution gave lower yields in the reduction process (**1f** *vs* **1g-h** and **1i** *vs* **1j**). When compounds with different halogen groups such as **1k** (F, Cl) and **1l** (F, Br) were used as substrates, good yields of 68% and 59% were obtained. Diphenylmethanols bearing electron-donating methyl groups such as methyl (**1m**) and methoxyl (**1n**) gave the yields of 93% and 24%, respectively, however compared with methyl substituent **1m**, dramatically decreased yields were observed by using diphenylmethanol bearing electron-withdrawing trifluoromethyl (**1o**) and ester (**1p**) groups. Naphthalene derivatives (**1q**) worked well providing the corresponding product in 76% yield. Interestingly, triphenylmethanol (**1r**) and triphenylmethanthiol (**1s**) gave rise to triphenylmethane in 95% and 91%, which suggests that thiol possesses the similar reactivity in this case. Despites many attempts, aliphatic alcohols and aromatic primary or secondary alcohols, did not undergo any reduction process and only adamantanol (**1t**) generated the corresponding adamentane in an isolated yield of 29%. Heterocyclic substrates (**1u and 1v**) were disable to give the dehydroxylation products. It is notable that prop-1-ene-1,1-diyldibenzene (**2w**) was obtained with 99% yield through β-H elimination when 1,1-diphenylpropan-1-ol (**1w**) was used as substrate, and 1,1-diphenylethanol (**1X**) only gave ethene-1,1-diyldibenzene (**2x**) in 55% yield (Scheme 2).
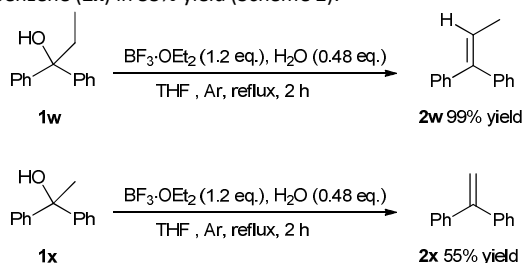
**Scheme 2** Investigation of 1,1-diphenylpropan-1-ol and 1,1-diphenylethanol.

Table 3 Substrate scope of diphenylmethyl ethers or esters[a]
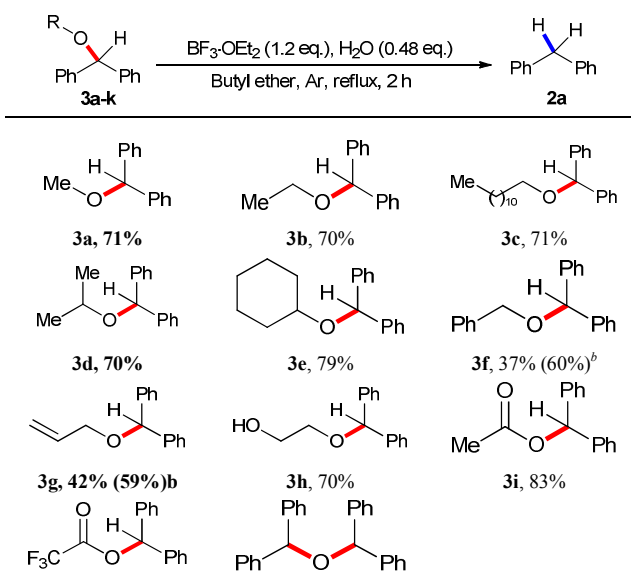

3j, 90%   **3k**, 60% (86%)[b]

[a] Conditions: **3** (1.0 mmol), BF$_3$·OEt$_2$ (1.2 mmol), H$_2$O (0.48 mmol), oil bath of 160 ^{o}C, butyl ether (1.0 mL) under argon for 2 h. Isolated yields. [b] BF$_3$·OEt$_2$ (2.4 eq.), H$_2$O (0.96 eq.), butyl ether (2.0 mL).

A series of leaving groups has been investigated in reductive reactions as well, such as alkoxy, hydroxymethoxy, acetyoxy groups (Table 3). The diphenylmethane was produced in yields ranging from 37-90% depending on the nature of the leaving group. Methoxy diphenylmethane **3a** provided the diphenylmethane in 71% yield. Regardless of linear (**3b**, **3c**), branched (**3d**) or cyclic (**3e**) alkoxy diphenylmethyl ethers employed, the reductive products were obtained in good yields. Benzyloxy (**3f**) and allyloxy (**3g**) substituted substrates gave similar levels of yields, 37% and 42% respectively, which was probably explained by the released benzylalcohol and allylalcohol which further trap the promoter BF$_3$·OEt$_2$ to form carbonium ion. Interestingly, when doubling the amount of BF$_3$·OEt$_2$ in these two cases, both yields were improved to 60% and 59%. The reaction of the hydroxyethyl substituted substrate (**3h**) led to **2a** in 70% yield, close to the yields obtained for alkoxy substitutions. Both acetoxy (**3i**) and trifluoroacetoxy (**3j**) were better leaving groups which resulted in yields of 83% and 90%. Diphenyl ether **3k** provided the diphenylmethane in 60% yield under standard conditions. Doubling the amount of BF$_3$·OEt$_2$ improved the yield to 86%.
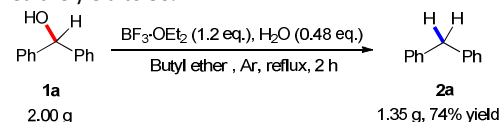
Scheme 3 Gram-scale synthesis.

A large-scale experiment was carried out to demonstrate both the practicality and effectiveness of our method. 74% yield of diphenylmethane (**2a**) was obtained when treating 2 g of **1a** under standard reaction conditions (Scheme 3).
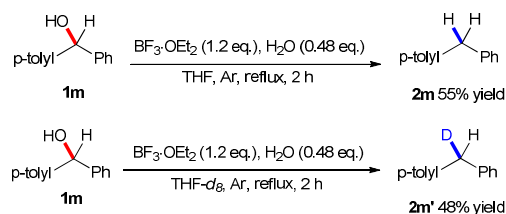
Scheme 4 Deuterated experiment.

Further experiments were performed to gain a better un-derstanding of the reaction mechanism. Deuterated experiments employing THF-d_8 were performed and the results showed the incorporation of the deuterium on the product 2m' and 92% of D on 2m', which was readily identified by 1H NMR analysis after silica column chromatography (Scheme 4). It is well-known that the p-σ hyperconjugation exists between the σ electron of α-H of ether and the lone pair electron on oxygen and hence the α-H could be activated through this p-δ hyperconjugation probably resulting in the formation of reductive hydrogen (H$^-$), accompanied with the formation of oxonium ion, which could react with another ether molecule to produce the reasonance stabilized species.[17c-h]

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Meanwhile, the diphenylmethyl cation could be produced in the presence of BF_3 from diphenylmethanol (**1**). The carbonium ion interacted with reductive hydrogen would give rise to alkane product (**2**).
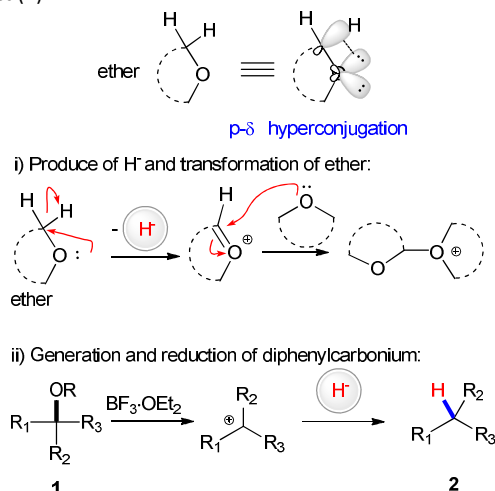

Figure 1 Proposed mechanism for reduction.

In summary, we have developed a novel ether/BF_3 reductive system for diphenylmethanols and their ether and ester derivatives, presenting a metal-free strategy and affording the corresponding alkane products in good to excellent yields for most cases. The *D*-labelled experiment showed the reductive hydrogen was generated from ethers. The favourable safety profile, ease to handling and environmentally benign nature make this methodology particularly attractive and practical.

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