Notes

Utility of Dysprosium Diiodide and Metallic Dysprosium as Reductants in Cyclopropanation Reactions of Alkenes with Dichloromethane

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Summary: We have found that the combination of dysprosium diiodide and dichloromethane can serve as an effective methylene transfer reagent for cyclopropanation of unfunctionalized alkenes. Furthermore, a Dy/I_2 system has also proved to be effective in the cyclopropanation of alkenes and CH_2Cl_2.

Introduction

The cyclopropanation of olefins is an important synthetic transformation because of the frequent existence of cyclopropane moieties in biologically active compounds[1,2] and their ability to undergo a wide range of reactions.[3] Among the various methods to produce cyclopropanated products, the Simmons−Smith reaction represents an attractive strategy.[4] There has been a growing effort in the past to develop modified procedures. Despite many exciting diverse metallic reagents having been developed,[5−10] the methylene halides employed are usually limited to CH_2I_2, CH_2Br_2, CH_2BrI, or $ClCH_2I$ depending upon the protocol used. Unfortunately, these effective and popular methylene halides are potentially unstable, expensive, and/or not easily available and alternatives are highly desirable.

It is known that $ClCH_2I$ instead of CH_2I_2 can lead to a better yield in the cyclopropanation of both allylic and α-allenic alcohols due to a more reactive carbenoid intermediate.[5h,9c,11] Despite the expectation that the decreased nucleofugacity of chloride ion relative to iodide ion would improve yield and selectivity, metal-induced cyclopropanation, wherein CH_2Cl_2 serves as a CH_2 partner, has remained largely unexplored. The significant limitation on the broad utility of CH_2Cl_2 often arises from its extreme stability, and this makes it a very common solvent in organic reactions. Recently, Yan and co-workers found that dichloromethane can serve as a novel electrophilic carbene equivalent for the enamine cyclopropanation and carbonyl methylenation promoted by $TiCl_4$−Mg.[8] However, this process does not generally extend to simple alkenes. Therefore, the search for a new entry of cyclopropanation from the CH_2Cl_2 precursor would be a highly valuable but challenging subject.

On the other hand, since the discovery of the "new" soluble divalent lanthanide diiodides LnI_2 (Ln = Nd, Dy, Tm), their utility in organic synthesis has received considerable attention.[12] These complexes have proven to be extraordinarily useful as powerful reductants and procatalysts in organic synthesis. For example, they can activate the inert C−Cl[13] and Si−Cl[14] bonds under mild conditions, which are difficult or even impossible to carry out in the SmI_2 system. However, to the best of our knowledge, no cyclopropanation and methylenation promoted by these "new" divalent lanthanide complexes have been reported. In continuation of our studies on the DyI_2 and Dy-

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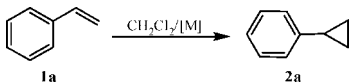(7) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Pine, S. H.; Zahier, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (c) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, *19*, 2417. (d) Lombardo, L. *Org. Synth.* **1987**, *65*, 81. (e) Hibino, J.; Okazoe, T.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5581. (f) Petasis, N. A.; Bzoweej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392.
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Table 1. Cyclopropanations of Styrene with CH₂Cl₂ in Different Conditions

entry	reductant	**1a**:M:CH₂Cl₂ (molar ratio)	solvent	temp (°C)	yield (%)[a]
1	DyI₂	1:2:1	THF	50	15
2	DyI₂	1:2:6	THF	50	63
3	DyI₂	1:2:10	THF	50	65
4	DyI₂	1:2.5:6	THF	50	77
5	DyI₂	1:2.5:6	THF	rt	40
6	DyI₂	1:2.5:6	THF	70	52
7	DyI₂	1:2.5:150	CH₂Cl₂	50	
8	DyI₂	1:2.5:6	toluene	50	
9	DyI₂	1:2.5:6	hexane	50	
10	SmI₂	1:3:6	THF	50	
11	Na	1:3:6	THF	50	
12	Zn	1:3:6	THF	50	
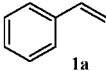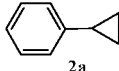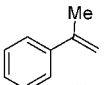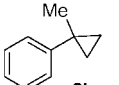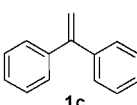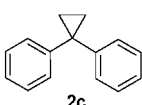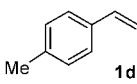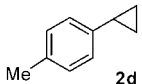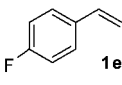
[a] GC yield based on styrene.

based synthetic transformations,[14,15] herein, we report two efficient dysprosium-based methods for cyclopropanation of unactivated alkenes under mild conditions using the most abundant and least expensive dichloromethane as the methylene transfer reagent.

Results and Discussion

Effecting the activation of CH₂Cl₂ should require highly reactive metallic species. Due to both the increased reducing power of DyI₂ relative to Mg and the higher chemical reactivity of samarium carbenoid compared with those based on zinc,[16] we postulated that the combination of DyI₂ and CH₂Cl₂ might exhibit chemistry that is complementary to the CH₂Cl₂–TiCl₄–Mg system, i.e., the production of cyclopropanated products by reaction with unactivated alken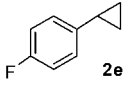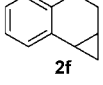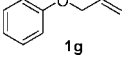es under mild conditions. The cyclopropanation of styrene and CH₂Cl₂ was chosen as a model reaction and was carried out in the presence of various metallic reagents under different reaction conditions to develop the optimum reaction conditions. Table 1 shows the representative results. The investigation results indicated that the yields depend strongly on the ratio of reagents and the reaction temperature. When the ratio of styrene, DyI₂, and CH₂Cl₂ was 1:2:1, the reaction could not proceed well (Table 1, entry 1). Increasing the amount of CH₂Cl₂ to the ratio of 1:2:6 (styrene:DyI₂:CH₂Cl₂) gave the cyclopropanation product (**2a**) in a moderate yield (63%, entry 2). Unceasingly increasing
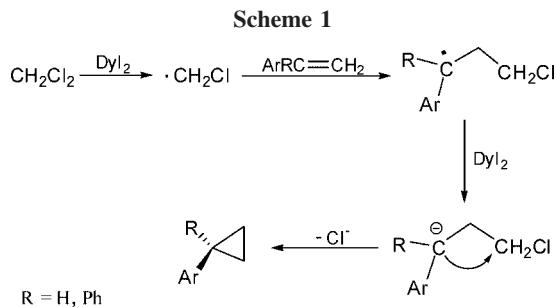
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Table 2. DyI₂ Promoted Cyclopropanation of Alkenes and CH₂Cl₂[a]

entry	alkene	product	isolated yield (%)
1	**1a**	**2a**	75
2	**1b** (Me)	**2b** (Me)	83
3	**1c**	**2c**	89
4	**1d** (Me)	**2d** (Me)	68
5	**1e** (F)	**2e** (F)	84
6	**1f**	**2f**	23
7[b]	**1g**		NR

[a] Reaction conditions: DyI₂ (2.5 mmol), alkene (1.0 mmol), CH₂Cl₂ (6.0 mmol), and THF (10 mL) at 50 °C for 6 h. [b] Recovered the starting material.

the amount of CH₂Cl₂ would not increase the yield remarkably (Table 1, entry 3). When the amount of DyI₂ was adjusted to 2.5 equiv to styrene, a satisfied result was acquired eventually (77%, entry 4). The yield was also affected by the reaction temperature, it decreased when lowering the temperature; for example, at room temperature with the same ratio of entry 4, the yield was only 40% (Table 1, entry 5), whereas a higher reaction temperature would lead to increase of the byproducts (Table 1, entry 6). Furthermore, we found the reaction achieved the highest yield in THF. However, no desired cyclopropanation product was obtained when the reaction was carried out in noncoordinated solvents such as CH₂Cl₂, toluene, and hexane (Table 1, entries 7–9). In addition, if DyI₂ was replaced by SmI₂, Na, or Zn, the reaction did not take place (Table 1, entries 10–12). The results indicated that DyI₂ plays a key role in the cyclopropanation reaction.

A series of olefins were subjected to the above optimal reaction conditions. The results of these experiments are presented in Table 2. The reactivity of olefins is controlled by the steric and electronic properties of the substituents. Among the various alkenes studied, terminal alkenes were found to be most reactive (Table 2, entries 1–5). The electron-donating groups, such as methyl, in the para position of the phenyl ring seemed to negatively affect the yield of the reaction (entry 4), while the electron-withdrawing groups, such as fluoride, in the para position seemed to positively affect the yield of the reaction, giving the corresponding substituted cyclopropane in a good yield (84%, entry 5). This is different from the previous observation in the In–CH₂I₂ system, wherein aromatic substituted alkenes possessing electron-donating groups were found to be more reactive.[10] We found among all the alkenes tested that 1,1-diphenylethylene gave the highest yield (entry 3), which

Scheme 1

R = H, Ph

may be due to the conjugated effect of the two phenyl groups. Cyclic alkene (**1f**) gave unsatisfactory results (entry 6).

The "heteroatom-directed" transformations are a well-established strategy for controlling chem- and stereoselectivity in organic synthesis.[17] Typically, allylic alcohols and ethers are significantly more reactive than simple alkenes for other metal carbenoid-based cyclopropanation.[5d,e,9,18,19] In marked contrast to these previous observations, surprisingly, the cyclopropanation reaction of 3-phenoxy propene did not take place in the present system even at prolonged reaction time or at elevated temperature, and the starting material **1g** was recovered (Table 2, entry 7). Furthermore, only one cyclopropanated product (**2a**) was isolated when a mixture of **1a** and **1g** was treated by the DyI$_2$/CH$_2$Cl$_2$ system.

On the basis of these observations, an alternative pathway for the reaction is proposed in Scheme 1. First, DyI$_2$ reacted with CH$_2$Cl$_2$ to generate chloromethyl radical. Then this carbon-centered radical added to styrene from the less hindered side. After that, further one-electron reduction of the newly formed benzylic radical produced the benzylic anion.[20] Finally, the anion intramolecularly attacked the carbon adjacent to the chloride to close the ring, and the substituted cyclopropanes were obtained.

Lanthanide metals are stable in air, nontoxic, and cheap, and have strong reducing power. The finding that lanthanide metals can be expected to provide more powerful reductants for reactions which are difficult to carry out in the SmI$_2$ system under certain conditions prompts us to examine whether metallic Dy can be used instead of DyI$_2$ in the cyclopropanation reactions.[15,21] When a mixture of dysprosium metal and iodine was allowed to react with dichloromethane in the presence of styrene (**1a**), the Dy metal gradually dissolved and phenyl cyclopropane (**2a**) was obtained, indicating that a mixture of Dy and I$_2$ can be used instead of DyI$_2$ as a reductant during this reaction. As can be seen in the experiments varying the molar ratio of Dy/I$_2$ (Table 3), the yield of **2a** was dependent on the amount of iodine and both Dy and I$_2$ are essential for this cyclopropanation reaction (Table 3, entries 1–5). More remarkable is the observation that metallic Sm effected the cyclopropanation of **la** with CH$_2$Cl$_2$ in the presence of the appropriate amount of I$_2$ (Table 3, entry 11) but SmI$_2$ did not work well (Table 1, entry 8), indicating that for the present reaction a Sm/I$_2$ mixture is more active than "SmI$_2$". Further-

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Table 3. Comparison of the Cyclopropanation of Styrene with CH$_2$Cl$_2$ Mediated by Different Metals

entry	metal (mmol)	I$_2$ (mmol)	solvent	isolated yield (%)
1	Dy (2)	2	THF	11
2	Dy (2)	1	THF	55
3	Dy (2)	0.4	THF	78
4	Dy (2)	0.1	THF	15
5	Dy (2)		THF	NR
6[a]	Dy (2)	0.4	THF	30
7	Dy (2)	0.4	CH$_2$Cl$_2$	
8	Dy (2)	0.4	toluene	
9	Dy (2)	0.4	CH$_3$CN	
10	Dy (2)	0.4	hexane	
11	Sm (2)	0.4	THF	40
12	Mg (4)	0.4	THF	53
13	Na (4)	0.4	THF	
14	Zn (4)	0.4	THF	

a The reaction was carried out at room temperature.

Table 4. Dy−I$_2$ Promoted Cyclopropanation Reactions of Alkenes with CH$_2$Cl$_2$[a]

entry	alkene	product	isolated yield (%)
1	**1a**	**2a**	78
2	**1b**	**2b**	73
3	**1c**	**2c**	93
4	**1d**	**2d**	65
5	**1e**	**2e**	81
6	**1f**	**2f**	20

a Reaction conditions: dysprosium (2.0 mmol), iodine (0.4 mmol), alkene (1.0 mmol), CH$_2$Cl$_2$ (2.0 mL), and THF (8 mL) at 50 °C for 6 h.

more, it was found that magnesium metal (Mg^{2+}/Mg = −2.37 V), which has a reducing power similar to that of dysprosium metal (Dy^{3+}/Dy = −2.35 V), was also effective to the reaction (Table 3, entry 12), although the yield was lower than that achieved with Dy/I$_2$. However, Na and Zn were inefficient as reductants for the present reaction even with longer reaction time or at elevated temperature (Table 3, entries 13 and 14). A screening of solvents for the Dy/I$_2$ system revealed that THF is a suitable solvent.

Having determined the optimum reaction conditions, we investigated the generality of this process. As shown from Table 4, a variety of styrenes can be cyclopropanated by CH$_2$Cl$_2$ to give the corresponding products in moderate to excellent yields.

Conclusion

In summary, we have developed an efficient DyI$_2$-based method for producing substituted cyclopropanes from unactivated alkenes and CH$_2$Cl$_2$ under mild conditions. The results not only further demonstrated that DyI$_2$ as a very powerful one-electron reductant would be a fertile area since it proved to have a somewhat different reactivity compared with the traditional divalent lanthanide complexes, but also should provide an attractive alternative route to cyclopropanation. In addition, we found that a mixture of metallic Dy and 0.2 equiv of I$_2$ can replace DyI$_2$ in this process. Further development on this methodology is currently under way in our laboratory.

Experimental Section

All reactions were carried out under argon atmosphere with the standard Schlenk techniques. The solvents were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. Alkenes were purchased from Aldrich. All

liquid reagents were redistilled and degassed. DyI_2 was prepared by the literature procedures.[22] Metal Dysprosium (purity: >99%) was purchased from Yuelong Co. Ltd. (China) as an ingot and was filed to powder (30–60 mesh) prior to use, which then was directly used without chemical pretreatment. Dichloromethane was refluxed and distilled over CaH_2 under nitrogen immediately prior to use. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 operating at 400 MHz with TMS as internal standard. GC-MS were obtained on a Hewlett-Packard 6890/5973 instrument. Flash column chromatography was carried out with 300–400 mesh silica gel, using ethyl acetate/hexane as eluent. All products were identified by comparison with those of authentic samples.[23]

General Procedure for the Cyclopropanation of Alkenes with CH_2Cl_2 Promoted by DyI_2. A 50 mL Schlenk bottle was charged with DyI_2 powder (1.04 g, 2.5 mmol) and cooled to 0 °C. THF (10 mL), CH_2Cl_2 (6.0 mmol), and alkenes (1.0 mmol) were added in order. Then, the mixture was stirred at 50 °C (oil bath) for 6 h (monitored by GC). During the reaction procedure, the mixture slowly turned to a gray suspension. The reaction was then quenched with saturated sodium bicarbonate. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography to afford desired products.

General Procedure for the Dy/I_2 Mediated Cyclopropanation of Alkenes with CH_2Cl_2. To a 50 mL Schlenk bottle were added Dy powder (0.324 g, 2.0 mmol), I_2 (0.102 g, 0.40 mmol), CH_2Cl_2 (2 mL), and THF (8 mL). After being stirred for a moment, the

reaction mixture changed from red-purple to yellow and then alkene (1 mmol) was added. The reaction mixture was allowed to stir at 50 °C (oil bath) for 6 h. During the reaction procedure metal was slowly consumed and the mixture turned to a gray suspension. The reaction was quenched with saturated sodium bicarbonate. The mixture was extracted with acetic ether. The organic layer was separated, dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography to afford the desired cyclopropanated products.

Phenylcyclopropane (2a). ^1H NMR (400 MHz, $CDCl_3$) δ 6.98–7.19 (m, 5H), 1.78–1.85 (m, 1H), 0.62–0.67 (m, 2H), 0.79–0.89 (m, 2H). EI-MS: m/z 118 (M^+).

1-Methyl-1-phenylcyclopropane (2b). ^1H NMR (400 MHz, $CDCl_3$) δ 6.90–7.17 (m, 5H), 1.38 (s, 3H), 0.79–0.84 (m, 2H), 0.54–0.58 (m, 2H). EI-MS: m/z 132 (M^+).

1,1-Diphenylcyclopropane (2c). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15–7.28 (m, 10H), 1.30 (s, 4H). EI-MS: m/z 194 (M^+).

1-(4-Methylphenyl)cyclopropane (2d). ^1H NMR (400 MHz, $CDCl_3$) δ 6.96–6.98 (d, J = 8.0 Hz, 2H), 6.87–6.89 (d, J = 8.0 Hz, 2H), 2.21 (s, 3H), 1.64–1.71 (m, 1H), 0.79–0.84 (m, 2H), 0.54–0.58 (m, 2H). EI-MS: m/z 132 (M^+).

1-(4-Fluorophenyl)cyclopropane (2e). ^1H NMR (400 MHz, $CDCl_3$) δ 6.84–7.16 (m, 4H), 1.80–1.93 (m, 1H), 0.82–0.89 (m, 2H), 0.54–0.59 (m, 2H). EI-MS: m/z 136 (M^+).

2,3-Benzobicyclo[4.1.0]heptane (2f). ^1H NMR (400 MHz, $CDCl_3$) δ 6.99–7.26 (m, 4H), 2.45–2.61 (m, 2H), 2.08–2.15 (m, 1H), 1.87–1.93 (m, 1H), 1.67–1.76 (m, 1H), 1.49–1.58 (m, 1H), 0.82–0.86 (t, J = 6.8 Hz, 2H). EI-MS: m/z 144 (M^+).

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