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Bismuth (III) Based catalysed coupling reactions for the Iodonium ylides through in-situ methodology

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Abstract:

In the presence of nitromethane, a base, a hypervalent iodine molecule, and a Bismuth(III) catalyst, cyclic ethers are cleaved to generate nitromethoxy acetates in up to 81 percent isolated yields. The process is a three-component reaction involving an ether, a carbenoid formed from nitromethane, and a carboxylate group derived from a hypervalent iodine molecule.

Key words: Bismuth catalyst, nitro methane, Iodonium ylides, Cyclic ethers.

Introduction:

Iodonium ylides are a group of hypervalent iodine compounds that can be employed as metal carbenoids precursors. [1–6] Iodonium ylides, which are made from an active methylene molecule and a hypervalent iodine precursor, have gained popularity as synthetic diazo compounds. [7] Due to the improved stability of the corresponding ylides, they have traditionally been made from active methylene compounds with two electron-withdrawing groups. [5] The focus has so far been on cyclopropanation reactions in studies and applications of in situ produced iodonium ylides. [1–4,6,8–11] There have also been single occurrences of C–H insertion11 and a rearrangement by intramolecular production of an oxonium ylide12.

A carbene or carbenoid reacting with an ether can produce a variety of results. In addition to C–H insertion and other rearrangements13, there are reports of ether polymerisation[14,15] and ether cleavage by photolysis [16], as well as examples of Bi(III) catalysed ether cleavage using an alkylideneiodonium salt. [17] A method for cyclopropanation using an in situ produced iodonium ylide flanked by only one electron-withdrawing group was recently published. 18 We now show how this nitromethane-derived iodonium ylide may also be used in a new reaction with cyclic ethers.

THF was treated with nitromethane, bis(acetoxy)iodobenzene (PhI(OAc)2), a base, and a rhodium catalyst to produce 4-(nitromethoxy)butyl acetate 1. (Scheme 1). We began looking into this unusual three-part system. coupling reaction by doing a thorough screening and investigating the effects of various bases and catalysts on the reaction .the response (Table 1). PhI(OAc)2 was used in these investigations. THF (10.0 equiv), a base, and bismuth (1.0 equiv) (II). catalyst was used, as well as a huge amount of nitromethane (neat). added at the same time, and the reaction was allowed to stir 3 hours at room temperature All reagents were used in the same way received. We discovered that the yield of 1 was strongly reliant on the yield of 2. based on the base of choice, potassium fluoride, and The best yields come from potassium acetate. In addition, in 1 was the primary reaction in all of the reactions, regardless of the base product. Since PhI(OAc)2 was the only source of acetate accessible in the reaction mixture when non-acetate bases were utilised, the acetate group in 1 must come from bis(acetoxy)iodobenzene. This is the first example of an iodonium ylide reaction in which the carboxylate ligand on PhI(OAc)2 acts as a reactant and is integrated into the product, to our knowledge.

Table 1: Initial Screening:

Entry	catalyst	Catalyst loading (mol%)	Base	Equvi Base	Yield(%)
1	$Bi_2(esp)_2$	10	KF	1.0	71.5
2	$Bi_2(esp)_2$	5	KOAc	1.0	74.7
3	$Bi_2(esp)_2$	2.5	NaOAc	1.0	75.3
4	$Bi_2(esp)_2$	1	KF	2.2	64.1
5	$Bi_2(OOct)_4$	10	Na_2CO_3	2.2	63.6
6	$Bi_2(OOct)_4$	5	K_2CO_3	2.2	55.8
7	$Bi_2(OOct)_4$	2.5	MgO	2.2	55.5
8	$Bi_2(OOct)_4$	1	KF	2.2	31.2
9	$Bi_2(TMA)_4$	10	K_3PO_4	2.2	57.8
10	$Bi_2(OAc)_2$	10	K_2CO_3	2.2	42.5
11	$Bi_2(TFA)_4$	10	CsF	2.2	41.6

The ligands on the di bismuth core of the catalyst had a significant effect on the reaction result, as was obvious from the initial screening. As a result, the impact of various catalysts and catalyst loadings was extensively investigated (Table 2). For this and subsequent optimization studies, potassium fluoride was chosen as the starting point. Pd(OAc)2 and Cu(acac)2 failed to catalyse the creation of 1 (entries 12 and 13), whereas all of the Bi(III) catalysts tested catalysed the formation of 1. In the lack of a catalyst, ether cleavage did not occur. In the previously described cyclopropanation reaction with nitromethane, the bridging catalyst Bi2(esp)2 was the catalyst of choice. 18 This catalyst proved to be the most efficient once again, allowing for a minimal catalyst loading while still producing acceptable yields, (numbers 1–4) Even when the catalyst loading was reduced to 1 mol%, a yield of 64% was obtained (entry 4).

We began examining the effects of other parameters on the reaction once these components were determined. At first, all of the trials were carried out at room temperature. When the temperature was increased to 30 C, however, better results were obtained. There was small temperature dependence in the reaction; At 30 C, the results appeared to be more repeatable than at room temperature. A reaction time of 3 hours, which had been chosen at the outset, proved to be adequate. The yields were unaffected by increasing the reaction time to 7, 15, or 24 hours.

After 1 hour of reaction time, a 66 percent yield of 1 was obtained, compared to 75 percent after 3 hours. Extremely dry circumstances had little effect on yields, whereas 0.3 equiv of additional water completely stopped the reaction. Initially, we thought that 2 equiv of base was required. However, it was discovered that the reaction was catalytic in terms of base, and that as little as 0.6 equiv of potassium fluoride was required to get a high yield of 1 (Table 3, entry).

Both nitromethane and THF were initially used because they are both inexpensive and readily available. used in a disproportionately great amount Experiments have revealed that THF and nitromethane levels could be high. without reducing to 5 equiv and 10 equiv, respectively Table 3, items 6–8, have a considerable effect on yields. The It was impossible to minimise the concentrations of all three reagents. at the same time without affecting yield (Table 3). 12th entry). To lower the THF and nitromethane equivalents, The amount of potassium fluoride in the solution has to be at a certain level. a minimum of 1.0 equiv.

Table 2: Effect of catalyst and catalysts loading

Entry	**catalyst**	**Catalyst loading (mol%)**	**Yield of (1%)**
1	$Bi_2(esp)_2$	10	71.5
2	$Bi_2(esp)_2$	5	74.7
3	$Bi_2(esp)_2$	2.5	75.3
4	$Bi_2(esp)_2$	1	64.1
5	$Bi_2(OOct)_4$	10	63.6
6	$Bi_2(OOct)_4$	5	55.8
7	$Bi_2(OOct)_4$	2.5	55.5
8	$Bi_2(OOct)_4$	1	31.2
9	$Bi_2(TMA)_4$	10	57.8
10	$Bi_2(OAc)_2$	10	42.5
11	$Bi_2(TFA)_4$	10	11.5

Table 3: Effect of varying the amounts of reagents

Entry	**KF(Equv.)**	**THF(Equiv.)**	**MeNO2(Equiv)**	**Yield of (%)**
1	0.5	10	18.6	71.5
2	0.6	10	18.6	74.7
3	0.8	10	18.6	75.3
4	1.0	10	18.6	64.1
5	1.5	10	18.6	63.6
6	1.0	5	18.6	55.8
7	1.0	10	10	55.5
8	1.0	5	10	31.2
9	1.0	3	10	57.8
10	1.0	1	10	42.5
11	0.6	5	5	11.5

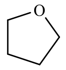
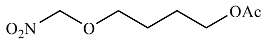
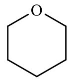
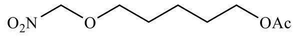
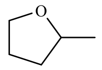
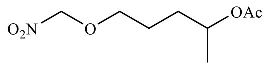
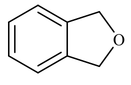
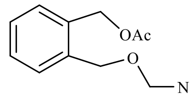
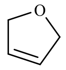
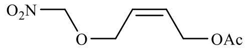
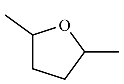
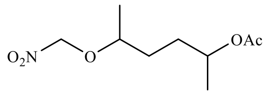
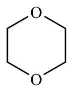
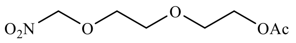
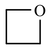
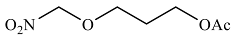
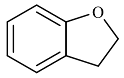
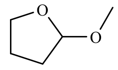
We investigated the effect of various hypervalent iodine compounds after establishing a good set of reaction conditions. The tests were carried out at 30 degrees Celsius with a catalyst loading of 2.5 mol% and reagent quantities as listed in Table 3, entry 8.

PhI(OPiv)2 produced 4-(nitromethoxy) butyl pivalate in a 57 percent yield, which is the corresponding product to 1. The carboxylate group in the product came from a hypervalent iodonium source, according to this result. There was no production of the TFA-derivative of 1 with PhI(TFA)2 as the hypervalent iodine molecule. The absence of a carboxylate substituent on iodine in iodo sylbenzene resulted in a complicated product combination.

A variety of cyclic ethers were exposed to the same reaction circumstances as reported in the previous studies to investigate the scope of the three-component coupling process. Table 4 illustrates the findings of this investigation, which included no attempts to improve the reaction conditions for the substrates in entries 2–10. THF produced the highest isolated yield, 71 percent. The yields on the other substrates were low to moderate. There was no discernible pattern in terms of which ethers are more easily cleaved in the reaction. 2-Methyl tetrahydrofuran (Table 4, entry 3) produced a 1.6:1 ratio of attack products at the 2- and 5-positions, favouring the product from attack at C-2. The double bond in the substrate 2,5- dihydrofuran provided a chance to see if ether cleavage or cyclopropanation was the favoured reaction.

Despite the fact that the reaction conditions were not dissimilar to those utilised before in the nitromethane cyclopropanation of olefins18, the reaction produced the ether cleavage product (Table 4, entry 5) and no cyclopropane. To see how changing the ring size affected the reactivity, it was also tested on THP (Table 4, entry 2). In a 55 percent yield, THP gave THF the equivalent product. Two chemicals were unable to form a three-component bond. There were no similar compounds to the rest of the series from 2-MeOtetrahydrofuran or 2,3-di-hydrobenzofuran. THF cleavage with nitromethane and PhI(OAc)2 has two possible molecular routes. Following the synthesis of an iodonium ylide from nitromethane and PhI(OAc)2, the corresponding ethereal oxonium ylide is catalysed by Bi(III).

Ring opening occurs when an acetate group attacks the oxonium ylide or the equivalent protonated oxonium ion. Given AcO's poor nucleophilicity and the presence of KF, a competitive assault by F rather than the acetate ion may have been expected. The result of such a reaction, however, was not discovered. Three products were identified and characterised when oxetane was used as the ether substrate (Table 4, item 8). (Scheme 3). Product 3 is generated via ring opening of the oxonium ylide or oxonium ion by acetate, and is analogous to the remainder of the series. Product 4 was likely formed when another molecule of trimethylene oxide opened the ring, forming a new oxonium ylide or ion that was then attacked by acetate. A formal Nef reaction of product 4 could explain the creation of product 5. The formation of products 4 and 5 may be due to the higher ring strain of trimethylene oxide compared to THF, A formal Nef reaction of product 4 could explain the creation of product 5. The creation of products 4 and 5 may be due to the increased ring strain of trimethylene oxide compared to THF, allowing nucleophilic attack and cleavage by other ether molecules through the ring opening of the trimethylene oxonium ylide or ion.

Entry	Substrate	Product	Yield
1.			85
2.			76
3.			82
4.			87
5.			77
6.			71
7.			56
8.			44
9.			
10.			

a Isolated yield after flash chromatography.,

b 1.6:1 ratio favouring the product of attack by AcO^- at C-2.

Conclusions:

To summarise, we used nitromethane and a hyper valent iodine molecule to establish a unique approach for cleaving a variety of cyclic ethers. The process is a three-component reaction that combines an ether with a carbenoid obtained from nitromethane and an acetate group derived from a hypervalent iodine molecule. This is the first time an in situ produced iodonium ylide has been shown to react intermolecularly to form a cyclic oxonium ylide. In the future, more research to widen the extent of the reaction will be revealed.

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