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Direct Organocatalytic Oxo-Metathesis, a *trans*-Selective Carbocation-Catalyzed Olefination of Aldehydes

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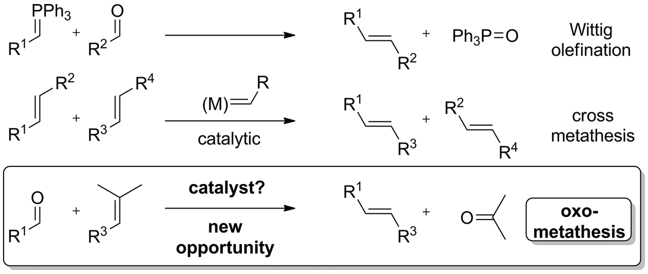
A direct organocatalytic carbonyl/olefin oxo-metathesis has been developed. The reaction is catalyzed by trityl tetrafluoroborate ($TrBF_4$) and utilizes unactivated alkenes for the olefination of aromatic aldehydes to give *trans* β-alkylstyrenes in yields of 44–85 % with only acetone as the byproduct. The pronounced Lewis acidity of the carbocation results in unusual reactivity that is proposed to catalyze a stepwise [2+2] cycloaddition to give an oxetane intermediate. Fragmentation of the latter in a formal retro [2+2] reaction gives the oxo-metathesis product.

Introduction

Alkenes are essential functional groups in organic chemistry, both as feedstock for further chemical transformations and as synthetic targets in their own right. Thus, chemical transformations leading to carbon–carbon double bond formation are of central importance in organic chemistry and carbonyl/ylide metathesis[1] (e.g., Wittig, Julia olefination) and olefin/olefin metathesis[2] reactions are examples of commonly used synthetic methods both in academia and industry. On the other hand, direct catalytic oxo-metathesis between an alkene and a carbonyl is a highly powerful complement to the strategies known today, and will open up new synthetic opportunities in particular with respect to atom economy and substrate scope (Scheme 1).[3–5] Despite the undisputable potential of this process, the carbonyl/olefin oxo-metathesis has rarely been reported in the literature and the development of a general catalytic and operationally simple strategy still remains a challenging task.[6]

The few reports on carbonyl/olefin oxo-metathesis known so far describe photochemically promoted [2+2]/retro[2+2] cycloadditions [Scheme 2, Equation (a)][7] and the use of stoichiometric amounts of Lewis acid[8] or a transition-metal complex,[9] which strongly limits the general applicability of the procedure in synthesis. Furthermore, attempts to establish catalytic oxo-metathesis processes have met with limited success and, to the best of our knowledge, there are only two known examples reported. In 2012, Lambert and co-workers developed an elegant organocatalytic ring-opening oxo-metathesis based on a [2+3]/retro[2+3] cycloaddition sequence [Scheme 2, Equation (b)].[3a] Unfortunately, the alkene was restricted to cyclopropene derivatives and opening of the three-membered ring was proposed to be the major driving force of this reaction.[4] Twenty years earlier, Bickelhaupt and coworkers reported two isolated examples of the direct olefination of benzaldehyde in the presence of a heterogeneous zinc(II) catalyst, EPZ-10 [Scheme 2, Equation (c)].[5,10] Under these conditions, the oxo-metathesis products, styrene and β-methylstyrene, were obtained in low yields.



Scheme 1. Double bond metathesis reactions.

Herein we present the further development of Bickelhaupt's strategy towards an operationally simple organocatalytic carbonyl/olefin oxo-metathesis. The reaction was applied to simple aromatic aldehydes and unactivated alkenes (amylene analogues) and is catalyzed by trityl tetrafluoroborate ($TrBF_4$) under mild reaction conditions.

Results and Discussion

Optimization of the Reaction Conditions

Recently our group has shown that trityl tetrafluoroborate ($TrBF_4$) is an efficient Lewis acid catalyst for several

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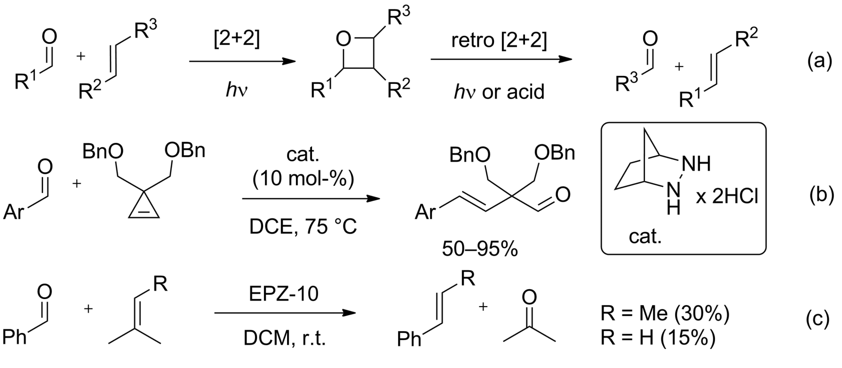


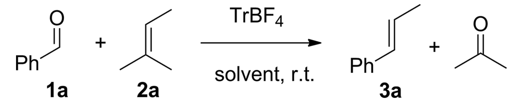
Scheme 2. Previous efforts toward carbonyl/olefin oxo-metathesis.

organic transformations (e.g., Diels–Alder, aza-Diels–Alder, conjugate addition, halogenation) and an interesting complement to traditional metal- or metalloid-catalyzed protocols.[11–16] In fact, the application of carbocations as Lewis acid catalysts is poorly studied and we reasoned that the carbocation might have properties different to those of metal- or metalloid-based Lewis acid catalysts. With this in mind we set out to evaluate the trityl cation in the reaction reported by Bickelhaupt and co-workers.[5] In our initial reaction, a 1:1 ratio of benzaldehyde (**1a**) and amylene (**2a**) in the presence of 7 mol-% trityl tetrafluoroborate ($TrBF_4$) gave the desired β-methylstyrene (**3a**) in 20% yield (Table 1, entry 1). Under these conditions the reaction stopped at 77% conversion with both unreacted aldehyde and olefin left in the reaction mixture. To push the reaction to completion we varied the ratio of the substrates. Increasing the amount of amylene (**2a**) resulted in the full conversion of benzaldehyde (**1a**) together with increasing amounts of unidentified byproducts and the yield of the product **3a** remaining low (Table 1, entries 2 and 3).[17] On the other hand, increasing the amount of benzaldehyde (**1a**) led to an increase in both the conversion and yield. Thus, using a 5:1 ratio of aldehyde **1a** to olefin **2a** gave the product **3a** in 43% yield (Table 1, entries 4 and 5).

The catalyst loading had a pronounced effect on the yield of the reaction and increasing the amount of $TrBF_4$ from 7 to 10 mol-% resulted in an increase in yield from 43 to 57% (Table 1, entries 5 and 6). The use of a 20 mol-% catalyst loading gave β-methylstyrene (**3a**) in 68% yield. Further increases in the catalyst loading had a less pronounced effect on the yield, with a 40 mol-% catalyst loading giving a yield of 75% (Table 1, entry 9). We compromised between catalyst loading and yield and settled on a 20 mol-% catalyst loading for further optimization.

The trityl cation is relatively unstable and even at gently elevated reaction temperatures (DCM at reflux) both the catalyst and amylene decomposed and no product formation could be observed by ^1H NMR spectroscopy of the crude reaction mixture. However, lowering the reaction temperature to –78 °C had a positive effect on the yield and β-methylstyrene (**3a**) was formed in 73% yield. However, a disadvantage was the increased reaction time from 31 h to more than 4 d before the full conversion of amylene (**2a**) was observed (Table 1, entry 8).

Table 1. Screening of the reaction conditions for the $TrBF_4$-catalyzed oxo-metathesis.[a]



Entry	Ratio [**1a**/**2a**]	$TrBF_4$ [mol-%]	Solvent	*t* [h]	Conv. [%]	Yield[b] [%]
1	1:1	7	DCM	100	77	20
2	1:2	7	DCM	100	99	18
3	1:5	7	DCM	100	100	23
4	2:1	7	DCM	100	85	34
5	5:1	7	DCM	100	100	43
6	5:1	10	DCM	31	100	57 (50)
7	5:1	20	DCM	31	100	68 (60)
8	5:1	20	DCM	100	100	73[c]
9	5:1	40	DCM	31	100	75 (59)
10	5:1	20	DCE	31	100	53
11	5:1	20	CH_3NO_2	31	100	55
12	5:1	20	CH_3CN	31	0	–
13	5:1	20	THF	31	0	–
14	5:1	20	Et_2O	31	0	–
15	5:1	20	PhMe	31	0	–

[a] The catalyst was added to a solution (0.3 M) of benzaldehyde (**1a**) and amylene (**2a**). [b] Determined by ^1H NMR analysis by using 1-methylnaphthalene as the internal standard. The yields given in parentheses are isolated yields. [c] Reaction performed at –78 °C.

The time course of the oxo-metathesis of amylene (**2a**) and benzaldehyde (**1a**) catalyzed by $TrBF_4$ reveals the fast consumption of the olefin with full conversion within 3 h (Figure 1). Surprisingly, after full conversion of amylene

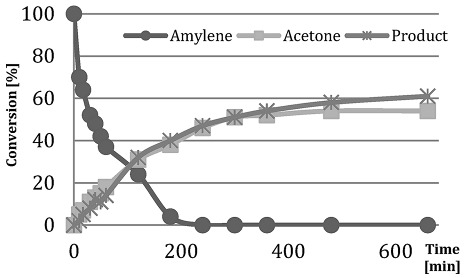


Figure 1. Reaction profile for the $TrBF_4$ (20 mol-%)-catalyzed oxo-metathesis of amylene (**2a**) and benzaldehyde (**1a**; 1:5 ratio of **2a**/**1a**). The yields were determined by ^1H NMR spectroscopy using 1-methylnaphthalene as the internal standard.

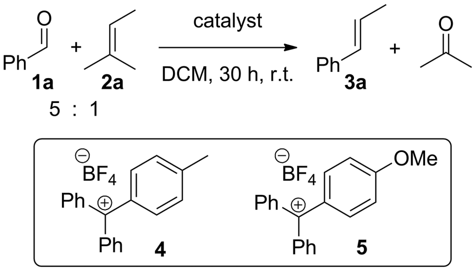
(**2a**), the yield of β-methylstyrene (**3a**; and acetone) is only 40% (cf. Table 1, entry 7). Interestingly, ^{1}H NMR analysis of the crude reaction mixtures over time revealed the build-up of two or more unidentified intermediates.[18] However, a prolonged reaction time led to a decrease of these intermediates and a slow increase of the product to give a yield of 68% over 30 h. It is also interesting to point out that the yield of acetone never deviates far from the yield of the product, which indicates that acetone does not undergo any aldol condensation reactions under these conditions (see Figure 1).[5] The high selectivity for the formation of the *trans* double bond as the only observable isomer should also be emphasized.

The solvent had a strong impact on the reactivity and coordinating solvents (CH_3CN and ethers) completely suppressed the reactivity, most likely due to blocking of the Lewis acidic site of the carbocation, and only starting material could be recovered (Table 1, entries 12–14). Nitromethane gave rather a high yield but a sluggish reaction with several unidentified byproducts observed in the crude ^{1}H NMR spectrum (Table 1, entry 11). $TrBF_4$ is poorly soluble in toluene, which most likely inhibits any reaction, and only starting material was recovered under these reaction conditions (Table 1, entry 15).

After establishing the optimal reaction conditions for the oxo-metathesis catalyzed by $TrBF_4$, we evaluated different Lewis acids. $BF_3{\cdot}OEt_2$ has been used before in intramolecular stoichiometric oxo-metathesis reactions[8] and Bickelhaupt and co-workers used a zinc catalyst immobilized on clay.[5] Interestingly, zinc(II) salts as well as $SnCl_4$ were completely inactive as catalysts under our conditions and both benzaldehyde (**1a**) and amylene (**2a**) remained unreacted (Table 2, entries 2–4), whereas the use of $InCl_3$ gave traces of product (Table 2, entry 5). On the other hand, $AlCl_3$ led to 78% conversion of amylene (**2a**) over 30 h, but again only traces of product were observed, most likely due to Lewis acid initiated polymerization (Table 2, entry 6). $BF_3{\cdot}OEt_2$ and $HBF_4{\cdot}OEt_2$ were found to be potent catalysts, although less efficient than the trityl ion, and gave the product in yields of 41 and 44%, respectively (Table 2, entries 7 and 8).

The trityl cation is a rather unique carbon-centered Lewis acid as its acidity can be readily tuned by variation of the electronic properties of the aromatic groups.[12,19] As expected, the oxo-metathesis became slower as the electron density of one of the aromatic rings increased (i.e., decreasing the Lewis acidity of the carbocation) on going from trityl to a mono-methyl- (**4**) to mono-methoxy-substituted (**5**) trityl cation (Table 2, entries 9–12). Unfortunately, decreasing the Lewis acidity of the trityl ion did not prevent any side-reactions and had a negative effect on the yield.

Table 2. Screening of Lewis acids for the $TrBF_4$-catalyzed oxo-metathesis.[a]



Entry	Catalyst (amount [mol-%])	Conversion [%]	Yield[b] [%]
1	$TrBF_4$ (20)	100	68
2	$ZnCl_2$ (20)	0	–
3	$Zn(OTf)_2$ (20)	0	–
4	$SnCl_4$ (20)	0	–
5	$InCl_3$ (20)	<5	trace
6	$AlCl_3$ (20)	78	7
7	$BF_3{\cdot}OEt_2$ (25)	100	41
8	$HBF_4{\cdot}OEt_2$ (30)	100	44
9	**4** (20)	75	21
10[c]	**4** (20)	100	45
11	**5** (20)	18	2
12[c]	**5** (20)	49	10

[a] The catalyst was added to a solution (0.3 M) of benzaldehyde (**1a**; 5 equiv.) and amylene (**2a**; 1.0 equiv.). [b] Determined by ^{1}H NMR analysis using 1-methylnaphthalene as the internal standard. [c] 100 h reaction time.

Scope and Limitations

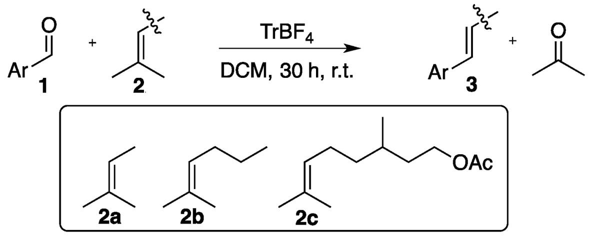
Following this we investigated the substrate scope of the oxo-metathesis reaction. This protocol tolerates different benzaldehydes although with some restrictions. Weakly electron-withdrawing groups, such as halogenated benzaldehydes (Cl, F, Br), gave the *trans* product **3** as the only observable isomer in yields of 54–59% (Table 3, entries 5, 6, and 8).

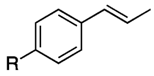
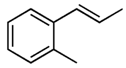
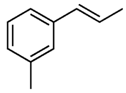
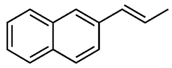
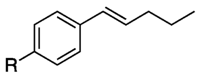
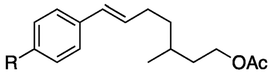
Weakly electron-donating groups, for example, *o*-, *m*-, and *p*-tolualdehyde as well as 2-naphthaldehyde, worked best in this transformation and gave the corresponding *trans* alkenes in yields of 55–85% (Table 3, entries 3 and 12–14). As was observed for the reaction of benzaldehyde (**1a**) and amylene (**2a**; Table 3, cf. entries 1 and 2), we also observed an improvement in yield for the reactions of *p*-tolualdehyde and *p*-fluorobenzaldehyde with amylene (**2a**) from 55 to 74% and from 59 to 66%, respectively, by decreasing the reaction temperature to –78 °C (Table 3, cf. entries 3 and 4, and 6 and 7). Unfortunately this was not a general trend and lowering the reaction temperature did not improve the yields of the reactions of *o*- or *m*-tolualdehyde or *p*-bromo- or *p*-chlorobenzaldehyde.

In most cases the β-alkylstyrenes are relatively unstable and in some cases volatile making them hard to isolate such that the isolated yields were in all cases substantially lower than the yields determined against internal standard.

Interestingly, for the strongly electron-donating substituent *p*-anisaldehyde, only traces of product could be observed by ^{1}H NMR analysis of the crude reaction mixture (Table 3, entry 9). However, full conversion of amylene and the formation of acetone corresponding to a yield of 60% was observed. This indicates that the corresponding oxo-metathesis product is indeed formed but is not stable under the reaction conditions and decomposes, most likely by

Table 3. Scope of the $TrBF_4$-catalyzed oxo-metathesis.[a]



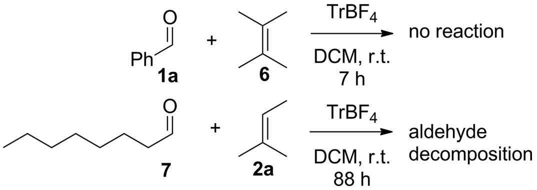
Entry	Product		Temp. [°C]	*t* [h]	Yield[b]
1		R = H	r.t.	30	68 (60)
2		R = H	–78	100	73
3		R = Me	r.t.	30	55 (52)
4		R = Me	–78	100	74
5		R = Cl	r.t.	30	54 (49)
6		R = F	r.t.	30	59 (49)
7		R = F	–78	100	66
8		R = Br	r.t.	30	55 (52)
9		R = OMe	r.t.	30	>5[c]
10		R = OMe	–78	30	15[c]
11		R = NO_2	r.t.	30	–[d]
12			r.t.	30	85
13			r.t.	30	83
14			r.t.	30	60 (54)
15		R = H	–20	135	44
16		R = Me	–20	135	36
17		R = F	–20	135	41
18		R = H	–20	135	51 (51)
19		R = Me	–20	135	47 (47)
20		R = Br	–20	135	44

[a] $TrBF_4$ was added to a solution (0.3 M) of aldehyde **1** (5 equiv.) and alkene **2** (1.0 equiv.). [b] Determined by ^1H NMR analysis using 1-methylnaphthalene as the internal standard. The yields given in parentheses are isolated yields. [c] Product decomposition. [d] Complex mixture, no product observed by crude ^1H NMR spectroscopy.

acid-catalyzed polymerization. By lowering the temperature to –78 °C, the decomposition of the product was somewhat diminished and *p*-methoxystyrene was obtained in 15% yield (Table 3, entry 10).[20] On the other hand, with the strongly electron-withdrawing *p*-nitrobenzaldehyde, the full conversion of amylene was observed to give a mixture of unidentified and unstable products (observed by ^1H NMR analysis of the crude reaction mixture) that decomposed upon attempted isolation (Table 3, entry 11). For this reaction, the formation of acetone could not be observed in the reaction mixture, which indicates that no oxo-metathesis product was formed.

Unfortunately, screening of different olefins turned out to be less productive. The oxo-metathesis of 2-methyl-2-hexene (**2b**) and citronellyl acetate (**2c**) with different benzaldehydes at room temperature gave the *trans* products with approximately one catalyst turnover, for example, yields of 24–35% were obtained. Both 2-methyl-2-hexene (**2b**) and citronellyl acetate (**2c**) turned out to be substantially less reactive than amylene (**2a**), and no reaction was observed at –78 °C. After extensive optimization the best reaction conditions for olefins **2b** and **2c** were found to be –20 °C for 135 h. Under these conditions the corresponding *trans* olefins were obtained in yields of 36–51% (Table 3, entries 15–20).

Surprisingly, the use of a tetrasubstituted olefin [e.g., 2,3-dimethyl-2-butene (**6**)] gave no reaction under the standard reaction conditions at room temperature and only starting materials could be recovered. On the other hand, aliphatic aldehydes, for example, octanal (**7**), decomposed under the same conditions and only amylene (**2a**) was recovered without any observable formation of the corresponding oxo-metathesis product (Scheme 3).

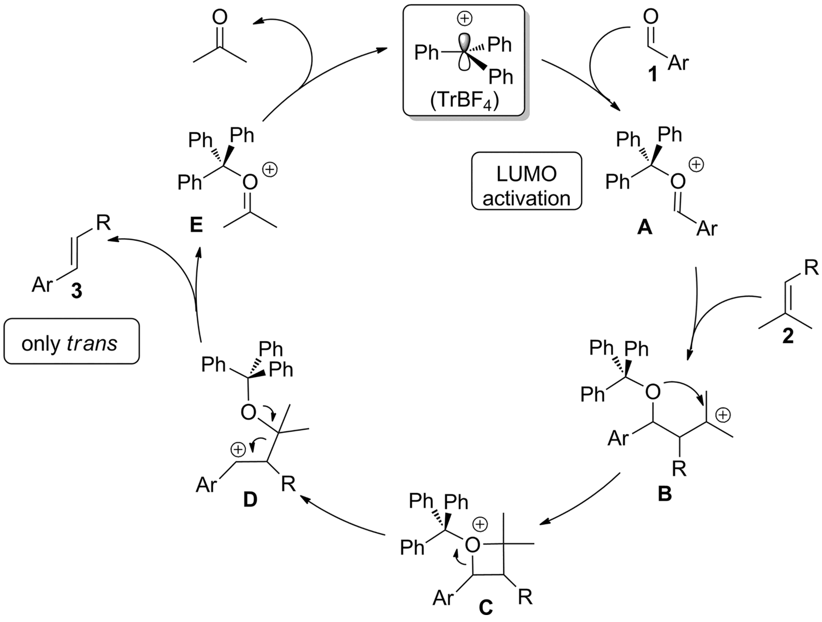


Scheme 3. Ineffective substrates for the $TrBF_4$-catalyzed oxo-metathesis.

Mechanistic Proposal

The mechanism for the oxo-metathesis, first proposed by Bickelhaupt and co-workers,[5] is believed to involve LUMO activation of aldehyde **1** with the formation of oxonium ion **A** (Scheme 4).

Nucleophilic attack of alkene **2** on the oxonium ion **A** gives tertiary carbocation **B**, which is analogous to the initial step of the Prins reaction.[21] The following step is believed to deviate from a normal Prins reaction and carbocation **B** is proposed to rapidly cyclize to give the oxetane intermediate **C** in an overall stepwise [2+2] cycloaddition. Opening of the oxetane ring generates the benzylic carbocation **D**, which undergoes a Lewis acid catalyzed fragmentation reaction to give acetone and the *trans* alkene.[22]



Scheme 4. Plausible mechanism for the trityl-catalyzed oxo-metathesis.

Conclusions

We have developed a mild organocatalytic carbonyl/olefin oxo-metathesis between readily available benzaldehyde derivatives and simple unactivated olefins. The reaction is operationally simple and uses cheap and readily available trityl tetrafluoroborate (TrBF$_4$) as a Lewis acid catalyst. Despite a relatively high catalyst loading and narrow substrate scope, the catalytic carbonyl/olefin oxo-metathesis is an important proof-of-concept for a reaction that predominantly relies on stoichiometric transition-metal reagents or photochemistry. In addition, we have demonstrated novel catalytic activity for the cheap and readily available tritylium ion. Although a highly interesting Lewis acid, this carbocation has received very little attention as a catalyst for organic transformations and the unusual reactivity demonstrated here shows the future potential of the carbocation as an environmentally friendly complement to traditional metal- and metalloid-based Lewis acid catalysts. We are continuing to explore the carbonyl/olefin oxo-metathesis reaction to obtain a deeper understanding of the mechanism and further extend the reaction scope towards a more general methodology. We are also continuing to explore the scope and limitations of carbocation catalysis to gain a greater understanding of its ability as a Lewis acid catalyst. These results will be reported in due course.

Experimental Section

General Procedure for the TrBF$_4$-Catalyzed Carbonyl/Olefin Oxo-Metathesis: Aldehyde **1** (5 equiv.) and alkene **2** (1 equiv.) were added to a solution of TrBF$_4$ (20.0 mol-%) in dichloromethane (c = 0.3 M with respect to the alkene) at the indicated temperature. After the indicated reaction time, the reaction mixture was quenched with saturated aq. NaHCO$_3$ and the resulting mixture was extracted with DCM (×3). The combined organic phases were dried with MgSO$_4$ and the solvent was distilled at ambient pressure. The residue was purified by silica gel column chromatography (pentane 100%) to give the *trans* β-alkylstyrenes **3**.

Acknowledgments

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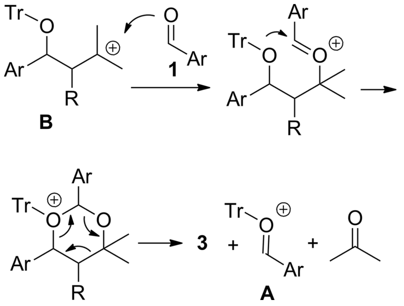
[22] An alternative mechanism, via the Prins reaction product,[5] involves addition of a second benzaldehyde **1** to intermediate **B** leading to the 1,3-dioxane intermediate **F**. Decomposition of the latter leads to the formation of **3**, **A**, and acetone.



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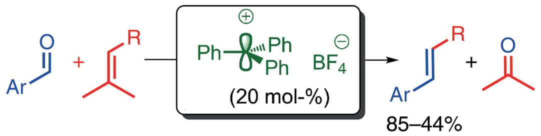
Oxo-Metathesis



A new partner in the metathesis dance: Trityl tetrafluoroborate ($TrBF_4$) catalyzes the direct oxo-metathesis of aldehydes and unactivated olefins to give β-alkylstyrene derivatives and acetone through an unusual metal-free formal [2+2]/retro [2+2] reaction sequence.

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Direct Organocatalytic Oxo-Metathesis, a *trans*-Selective Carbocation-Catalyzed Olefination of Aldehydes

Keywords: Organocatalysis / Metathesis / Carbocations / Ketones / Alkenes