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Formal [4 + 4]-, [4 + 3]-, and [4 + 2]-cycloaddition reactions of donor-acceptor cyclobutenes, cyclopropenes and siloxyalkynes induced by Brønsted acid catalysis[†]

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Brønsted acid catalyzed formal [4 + 4]-, [4 + 3]-, and [4 + 2]-cycloadditions of donor-acceptor cyclobutenes, cyclopropenes, and siloxyalkynes with benzopyrylium ions are reported. [4 + 2]-cyclization/deMayo-type ring-extension cascade processes produce highly functionalized benzocyclooctatrienes, benzocycloheptatrienes, and 2-naphthols in good to excellent yields and selectivities. Moreover, the optical purity of reactant donor-acceptor cyclobutenes is fully retained during the cascade. The 1,3-dicarbonyl product framework of the reaction products provides opportunities for salen-type ligand syntheses and the construction of fused pyrazoles and isoxazoles that reveal a novel rotamer-diastereoisomerism.

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Medium-sized rings are the core skeletons of many natural products and bioactive molecules,¹ and a growing number of strategies have been developed for their synthesis.² Because of their enthalpic and entropic advantages, ring expansion is a highly efficient methodology for these constructions.³⁻⁶ For example, Sun and co-workers have developed acid promoted ring extensions of oxetenium and azetidinium species formed from siloxyalkynes with cyclic acetals and hemiaminals (Scheme 1a).⁴ Takasu and co-workers have reported an elegant ring expansion with a palladium(II) catalyzed 4π -electrocyclic ring-opening/Heck arylation cascade with fused cyclobutenes (Scheme 1b).⁵ Each transformation is initiated by the formation of fused bicyclic units followed by ring expansion or rearrangement to give medium-sized rings.

Strategies for the formation of fused bicyclic compounds rely on cycloaddition of dienes or dipoles with unsaturated cyclic compounds⁷ and, if the reactant cyclic compound is strained and chiral, the resulting bicyclic compound is activated toward ring opening that results in retention of chirality. We have recently reported access to donor–acceptor cycloalkenes by [3 + n] cycloaddition that have the prerequisites of unsaturated cyclic compounds suitable for cycloaddition.⁸ Donor–acceptor (D–A) cyclopropenes⁹ and cyclobutenes¹⁰ have sufficient strain in the resulting bicyclic compounds to undergo ring opening. We envision that the selection of a diene or dipolar reactant and suitable reaction conditions could realize cycloaddition and subsequent ring expansion. Benzopyrylium species,^{11,12} which are generated by metal or acid catalysis, have attracted our attention. We anticipated that their high reactivity would overcome the conventional unfavorable kinetic and/or

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b) Ring expansion/Heck arylation reaction of fused cyclobutenes



c) This work: [4+2] cyclization/ring expansion reactions



Scheme 1 Cycloaddition/ring expansion background and this work.

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 $78(76)^{d}$

62

50

thermodynamic factors that typically impede medium-sized ring formation. From a mechanistic perspective, benzopyrylium species are often formed by transition metal catalyzed reactions with 2-alkynylbenzaldehydes.¹¹ Recently, the reaction between 1*H*-isochromene acetal and Brønsted acid catalyst forms the 2-benzopyrylium salts that could react with functional alkenes to give same cycloaddition products.¹² Consequently, we believed that the [4 + 2]-cyclization between benzopyrylium species and donor–acceptor cyclobutenes, cyclopropenes, or siloxyalkynes would give bridged oxetenium intermediates, which contain high strain energy that should provide the driving force for ring expansion. The "push and pull" electronic effect of donor–acceptor functional groups facilitates deMayo-type ring-opening of the cyclobutane or cyclopropane skeletons (Scheme 1c).¹³

Here we report bis(trifluoromethanesulfonyl)imide (HNTf₂) catalyzed formal [4 + 4]-, [4 + 3]- and [4 + 2]-cycloaddition reactions of D–A cyclobutenes, cyclopropenes, and siloxyalkynes with benzopyrylium salts. Polysubstituted benzo-cyclooctatrienes, benzocycloheptatrienes and 2-naphthols, are produced in good to excellent yields and selectivities. Complete retention of configuration occurs using chiral cyclobutenes, and opportunities for further functionalization are built into these constructions.

Initially, we conducted transition metal catalyzed reactions with 2-alkynylbenzaldehyde intending to produce the corresponding benzopyrylium ion and explore the possibility of cycloaddition/ring opening with donor-acceptor cyclobutene **2a**. Use of $Ph_3PAuCl/AgSbF_6$, $Pd(OAc)_2$ and $Cu(OTf)_2$, which were efficient catalysts in previous transformations,¹¹ gave only a trace amount of cycloaddition product (Fig. 1). Spectral analysis showed that mostly starting material remained (Fig. 1-i and ii). Increasing the reaction temperature led only to decomposition of 2-alkynylbenzaldehyde (Fig. 1-iv) or donor-acceptor cyclobutene **2a** (Fig. 1-iv).

From these disappointments we turned our attention to 1*H*isochromene acetal **1a** as the benzopyrylium ion precursor. Various Lewis acid catalysts were employed with limited success, but we were pleased to observe the formation of the desired formal [4 + 4]-cycloaddition benzocyclooctatriene product **3aa**, albeit in low yields (Table 1, entries 1–6). Selection of the Brønsted super acid HNTf₂ (ref. 14) proved to be the most promising, producing **3aa** in 40% yield (Table 1, entry 7). Increasing the amount of D–A cyclobutene **2a** by 30% gave a much higher yield of **3aa** (Table 1, entry 8 *vs.* 7). Optimization of the stoichiometric reaction between **1a** and **2a** by increasing



Fig. 1 Reaction of 2-alkynylbenzaldehyde with donor-acceptor cyclobutene 2a.

Table 1 Optimization of reaction conditions^a

HNTf₂

HNTf₂

HNTf₂

90

 $10^{c,e}$

 $11^{c,f}$



^{*a*} Reactions were performed by adding the catalyst (10 mol%) to **1a** (0.1 mmol) and **2a** (0.1 mmol) in CH₂Cl₂ (2 mL) at the corresponding temperature for 24 h. ^{*b*} Yields were determined by ¹H NMR spectroscopic analysis with CH₂Br₂ as the internal standard. ^{*c*} 1.3 equiv. **2a** was used. ^{*d*} Isolated yield. ^{*e*} Reaction performed at 60 °C for 12 h. ^{*f*} 5 mol% catalyst loading.

35

60

35

the reaction temperature from rt to 35 °C led to the formation of the desired product in 76% isolated yield (Table 1, entry 9 *vs.* 8). However, a further increase in the reaction temperature (Table 1, entry 10) or reducing the catalyst loading to 5 mol% did not improve the yield of **3aa** (Table 1, entry 11).

With optimized conditions using 1a in hand, we examined the scope of the formal [4 + 4]-cycloaddition reactions of D–A cyclobutenes 2 with a diverse set of acetal compounds 1. As shown in Scheme 2, a wide range of acetal substrates (1a–1i) with different substituents at different positions all reacted



Scheme 2 Scope of the [4 + 4]-cycloaddition reaction of D–A cyclobutenes and 1*H*-isochromene acetals.^{*a*} ^aReactions were performed by adding HNTf₂ (10 mol%) to 1 (0.1 mmol) and 2 (0.13 mmol) in CH₂Cl₂ (2 mL) at 35 °C for 24 h. Isolated yields are reported.

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smoothly with D–A cyclobutene **2a** to form the corresponding benzocyclooctatriene products **3** in good to excellent yields. Structural variations in the acetals produced only modest changes in product yields which ranged from 55 to 87%. Similarly, both electron-withdrawing and electron-donating substituents at the 4-position of the cyclobutene phenyl ring produced the corresponding products (**3db–3dd**) in good yields, and 2-naphthyl (**2e**) and 2-thienyl (**2f**) substituted cyclobutenes were suitable substrates (85% and 51% product yields, respectively). *trans*-1,2,3,4-Tetrasubstituted ($R^2 = CH_3$) 2-siloxycyclobutenecarboxylate **2g** also underwent [4 + 4]cycloaddition with **1d** in good yield and fully retained its diastereoselectivity. The structure of **3fa** was confirmed by X-ray diffraction (Scheme 2).¹⁵

Chiral donor-acceptor cyclobutenes with high enantiomeric excess and diastereoselectivity are conveniently obtained by catalytic [3 + 1]-cycloaddition of enoldiazoacetates with acyl ylides of sulfur.¹⁰ To determine if optical purity is retained, chiral D-A cyclobutene 2a (80% ee) was reacted with 1d under the optimized conditions, and the corresponding benzocyclooctatriene product 3da was obtained in good yield with complete retention of configuration (Scheme 3, eqn (1)). With trans-disubstituted 2g and 2h that have higher optical purity, however, 3dg and 3dh were obtained in moderate yields with full retention of diastereo- and enantioselectivities, but addition products 8dg and 8dh were formed competitively (Scheme 3, eqn (2)). These compounds resulted from initial addition then desilvlation, indicating that the [4 + 2]-cyclization is a stepwise reaction. Attempts to suppress the competing pathway by changing solvents or using the isopropyl acetal substrate to form a bulky 2-propanol nucleophile (1j) failed (for details, see ESI \dagger). However, *p*-methoxy (\mathbb{R}^1) substituted **1g** that would stabilize the incipient benzopyrylium ion gave higher selectivity (4: 1 vs. 2: 1), and the desired [4+4] cycloaddition product 3gg was isolated in 50% yield with 97% ee and >19 : 1 dr (Scheme 3, eqn (3)).

To further expand the generality of this strategy, we investigated its use with donor-acceptor cyclopropenes 4. The desired

HNTf₂ (10 mol%)

DCM 35 °C 24 h

H₂CO₂(

. СОРһ

= CH₃, >19:1 dr, 97% ee = Et, >19:1 dr, 90% ee;

COPh

H₃CO₂

H₃CO₂

2g, >19:1 dr, 97% ee

осн.

осн₂

 $Ar = p-CH_3OC_6H_4$

1q

COP

HNTf₂ (10 mol%)

HNTf₂ (10 mol%) DCM, 35 °C, 24 h

DCM, 35 °C, 24 h

PhOC

(1)

hOC

8dg, R = CH₃, 23% yield, 5:1 di

PhOC CH3

8gg, 12% yield

189

8dh R = Et

(2)

1 di

(3)

'COP

\ СО₂СН₃

3dg:8dg = 2:1

3dh:8dh

3da, 81% yield, 80% ee PhOC OH

''COPh

1 dr, 97% ee

90%

-CH

'COPh

CO2CH3

: CĤ

= Et,

CU₂C... 3gg, 50% yield, >19:1 dr, 97% ee 3gg:

ArOC OH





Scheme 4 Scope of the [4 + 3]-cycloaddition reaction of D–A cyclopropenes and 1*H*-isochromene acetals.^{*a*} ^aReactions were performed by adding HNTf₂ (20 mol%) to **1** (0.2 mmol), **4** (0.24 mmol) and 4 Å (50 mg) in CH₂Cl₂ (2 mL) at rt for 2 h. Isolated yields are reported.

formal [4 + 3]-cycloaddition products **5** were obtained in good to excellent yields (Scheme 4). Optimized conditions used 20 mol% HNTf₂ catalyst with 4 Å molecular sieves at room temperature for 2 h. The scope of this [4 + 3]-cycloaddition reaction with cyclopropenes **4** showed that acetals bearing both electron-donating and electron-withdrawing substituents on the aromatic ring were tolerated. However, as with [4 + 4]cycloaddition reactions, the [4 + 3] reactions of **1** with R^1 = alkyl or H did not produce any of the desired products. Furthermore, 3-substituted cyclopropenes **4b**-**4d** participated in this reaction, and their products (**5ab**-**5ad**) were obtained in 63%-81% yields.

Siloxyalkynes 6, as electron-rich alkynes, have been widely used in diverse cyclization reaction.4,16 We expected that 6 could also participate in [4 + 2]-cyclization/ring-expansion cascade processes, giving substituted 2-naphthol products. Interestingly, substituent controlled diverse products were obtained in good to excellent reactivity and selectivity (Scheme 5). Aryl (R^{1}) substituted acetals (1a-1d, 1f, 1h, 1i) reacted with siloxyalkynes 6a-6d, giving 2-naphthols (7aa-7ad and 7ba-7ia) in 35%-96% yields. With electron-donating group (EDG) substituents (7ba and 7ca) on the aromatic ring, higher reactivity was observed relative to those with electron-withdrawing groups (7da-7ia). In addition, the acetal with $R^1 = H(1m)$ reacted with siloxyalkynes 6 to form the 2-naphthol-1-carboxaldehyde derivative in good yield, and the structure of 7ma was confirmed by X-ray diffraction (Scheme 5b).¹⁵ Intriguingly, the *n*-butyl (R¹) substituted acetal **1n** reacted with siloxyalkynes *via* a [4 + 2]-cyclization with loss of methyl pentanoate (BuCO₂CH₃), affording siloxy naphthalenes 7na-7nd that are important precursors to the widely used axially chiral 2,2'-binols.17 The substrate scope of siloxyalkynes 6 for their formal [4 + 2]-cycloaddition reaction with *n*butyl substituted acetal 1n was also explored (Scheme 5c). In all cases methyl pentanoate was eliminated to form 2,3-disubstituted naphthalene products (7na-7nd). Alkyl substituted siloxyalkynes (6a-6c) showed higher reactivity compared with phenyl substituted siloxyalkynes 6d. It should be mentioned that, recently, a similar transformation using $BF_3 \cdot OEt_2$ as catalyst or in excess (2 equiv.) with 2,4,6-collidine (1 equiv.) was reported,18



Scheme 5 Scope of the [4 + 2]-cycloaddition reaction of siloxvalkynes and 1*H*-isochromene acetals.^a Reactions were performed by adding HNTf₂ (10-30 mol%) to 1 (0.2 mmol) and 6 (0.3-0.4 mmol) in CH₂Cl₂ (2 mL) at rt for 10 min. Isolated yields are reported. ^b40 mol% HNTf₂ catalyst was used.

and HNTf₂ was stated to be much less effective. To clarify this discrepancy, we carefully repeated these transformations (7ma and 7na) and found that all starting materials are completely consumed in less than 10 min to deliver [4 + 2]-cycloaddition products in good yields. Prolonging the reaction time to 12 hours, which was the reaction time used by the authors, results in their decomposition to a complex mixture of materials.

To illustrate the utility of this process, a large scale catalytic [4 + 4] cycloaddition was performed, and adduct 3da was



Fig. 2 Large scale reaction, further transformations, and ligands synthesis



obtained in 87% vield. Further transformations were conducted for the synthesis of pyrazole and isoxazole structures based on its 1,3-dicarbonyl skeleton (Fig. 2a). Compound 3da reacted with hydrazine and hydroxylamine in refluxed ethanol, affording pyrazole 14da and isoxazole 15da in 89% yield or 66% yield, respectively. The structure of 15da was confirmed by X-ray diffraction.15 Interestingly, two NMR distinguishable interconvertible diastereoisomers were detected for each of these eightmembered cyclic products (2.5:1 and 5:1 dr for 14da and 15da, respectively, in CDCl₃). These diastereoisomers are rotamers (for details, see ESI[†]) that exist at equilibrium with each other in solution but form one crystalline product (X-ray structure of 15da). In addition, the cycloaddition product 7ma reacted with chiral 1,2-cyclohexanediamine and 1,2-diphenylethylenediamine to give salen-type ligands L1 and L2 in 53% yield and 74% yield, respectively, which provides new opportunities for ligand screening (Fig. 2b).19

In the mechanistic possibility considered for these HNTf₂ catalyzed cycloaddition reactions (Fig. 3), protonation of acetal 1 with HNTf₂ gives the corresponding highly reactive benzopyrylium intermediate int-I, which reacts with donor-acceptor cyclobutenes 2, cyclopropenes 4, or siloxyalkynes 6 affording addition intermediates int-II that undergo ring closure to int-**III.** Ring expansion then occurs to deliver 3, 5 and 7 in good to excellent yields with fully retained stereoselectivities. Furthermore, the formed TIPSNTf₂ ([4 + 4]- and [4 + 3]-cycloaddition) or $HNTf_2$ {[4 + 2] cycloaddition} are active acid catalysts for the conversion of 1 to benzopyrylium intermediate int-I that continues the catalytic cycle. With sterically larger D-A cyclobutenes or when a less ring-strained benzocyclopentene 12 is employed (for details, see ESI[†]), the competing direct desilylation of int-II occurs, delivering addition byproducts 8 or 13. Compounds 7na-7nd arise from the analog to int-III from which ketene formation or methanol displacement effects 1,4elimination.

Conclusions

In summary, we have realized formal [4 + 4]-, [4 + 3]-, and [4 + 2]cycloaddition reactions of D-A cyclobutenes, cyclopropenes,

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and silyloxyalkynes *via* Brønsted acid catalysis that are not feasible *via* the alternative metal catalysed process. The success of these transformations is attributed to the design of the [4+2]cyclization/deMayo-type ring-expansion cascade processes in which various benzocyclooctatrienes, benzocycloheptatrienes and 2-naphthols are obtained in good to excellent yields and selectivities. In addition, the optical purity of the reactant donor–acceptor cyclobutenes is fully retained. The cycloaddition products provide additional opportunities in salen-type ligand synthesis and heterocyclic synthesis exemplified by the formation of pyrazole and isoxazole products.

Conflicts of interest

There are no conflicts to declare.

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