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# TfOH promoted reactions of vinyl *gem*-dichlorocyclopropanes with arenes: access to aryl *gem*-dichloropentenes

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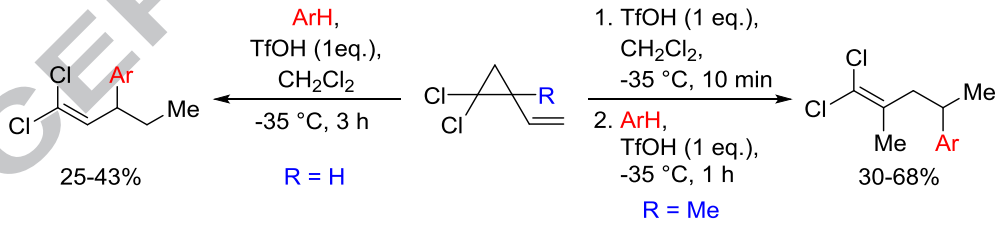
**Keywords:** 1,1-dichlorocyclopropanes, 1,1-dichloroalkenes, triflic acid, Friedel-Crafts reaction, carbocations

## Graphical Abstract




## Abstract

The reaction of 1,1-dichloro-2-vinylcyclopropane with arenes under the action of the superacid TfOH afforded 3-aryl-1,1-dichloropent-1-enes (25-43% yield), as the products of cyclopropane ring opening. The reaction of 1,1-dichloro-2-methyl-2-vinylcyclopropane was realized as a two-step procedure, including initial *in situ* generation of the corresponding triflate, 5,5-dichloro-4-methylpent-4-en-2-yl trifluoromethanesulfonate, from the cyclopropane and TfOH, followed by reaction with arenes and TfOH to give 1,1-dichloro-2-methyl-4-arylpent-1-enes (30-68% yield).

1,3-Butadiene and isoprene are important by-products[1] of petrochemical synthesis which are used for the production of synthetic rubbers, thermoplasts, and other materials.[2] These dienes easily react with dichlorocarbene to form vinyl substituted *gem*-dichlorocyclopropanes,[3] which are important intermediates in organic synthesis.[4] Electrophilic activation of *gem*-dihalocyclopropanes represents one of the methods for carbon-carbon bond formation involving these compounds.[5,6] Previously, we have shown that the $AlCl_3$-catalyzed reactions of chloromethyl- and 2-bromo-2-phenyl- *gem*-dichlorocyclopropanes with arenes led to 1,1-dichloroalkenes.[5] Due to the functionalization of the $CCl_2$-group, these *gem*-dichloroalkenes participate in the formation of chloroalkenes, acetylenes,[7,8] allenes,[9] and heterocycles.[10]

The main goal of this work was to study the reactions of vinyl substituted *gem*-dichlorocyclopropanes with arenes in the presence of Brønsted acids using two vinyl *gem*-dichlorocyclopropanes **1a** and **1b**, obtained from butadiene-1,3 and isoprene, respectively (Fig. 1).

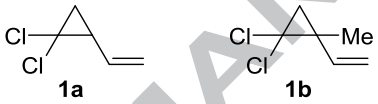
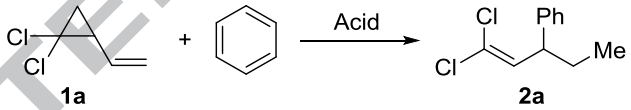



**Figure 1.** Examined vinyl gem-dichlorocyclopropanes **1a** and **1b**.

**Table 1.** Brønsted acid-promoted reaction of **1a** with benzene.



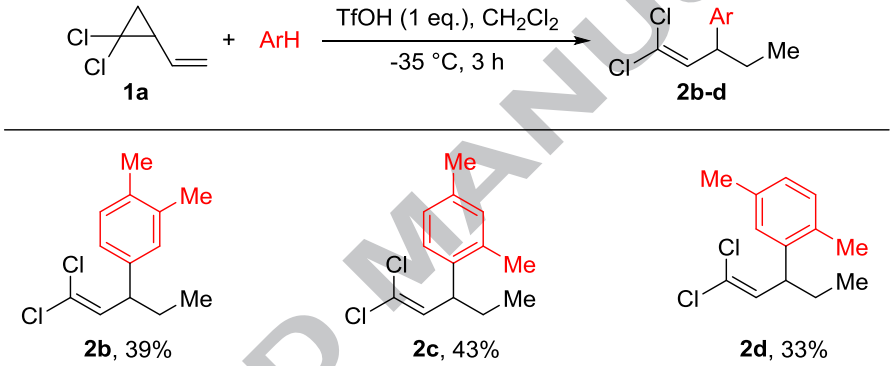

| Entry | Reaction conditions | | | | Yield **2a** (%) |
|---|---|---|---|---|---|
| | Acid | Ratio of **1a** : PhH : acid | Temperature (°C) | Time (h) | |
| 1 | TfOH | 1 : 3 : 50 | 20 | 1 | oligomers |
| 2 | TfOH[a] | 1 : 3 : 50 | -35 | 1 | oligomers |
| 3 | TfOH[a] | 1 : 3 : 1 | -35 | 1 | 13 |
| **4** | **TfOH[a]** | **1 : 3 : 1** | **-35** | **3** | **25** |
| 5 | $H_2SO_4$ | 1 : 50 : 5 | 20 | 9 | 15 |
| 6 | $CF_3CO_2H$ | 1 : 50 : 5 | 20 | 24 | no reaction |
| 7 | $FeCl_3$ | 1 : 50 : 1 | 20 | 1 | oligomers |
| 8 | $AlCl_3$ | 1 : 50 : 1 | 20 | 1 | oligomers |

[a]Solvent $CH_2Cl_2$.

First, we explored the reactions of cyclopropane **1a** with benzene in the presence of various Brønsted or Lewis acids (Table 1). It was found that the main reaction product, 1,1-dichloro-3-phenylpent-1-ene (*gem*-dichloropentene) **2a**, was formed as a result of cyclopropane ring opening.

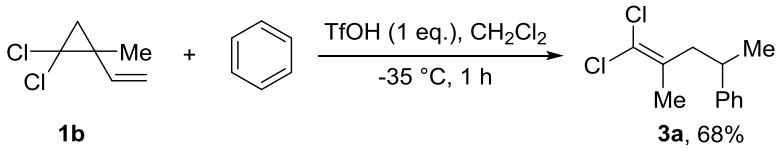
Among the acids examined, the best results were obtained using TfOH (1 equiv.) in $CH_2Cl_2$ at -35 °C for 3 h, to give **2a** in 25% yield (Entry 4). Increasing the reaction time at -35 °C did not lead to a higher yield of **2a**. The use of larger amounts of TfOH gave rise to oligomeric compounds (Entries 1, 2), due to cationic oligomerization of the initially formed **2a**. Other Brønsted acids $H_2SO_4$, $CF_3CO_2H$ (Entries 5, 6) or Lewis acids $FeCl_3$, $AlCl_3$ (Entries 7, 8) did not give satisfactory results in this reaction.

Having the optimal conditions in hand (1 equiv. TfOH, $CH_2Cl_2$, -35 °C, 3 h), we synthesized *gem*-dichloropentenes **2b-d** from **1a** and isomeric xylenes in moderate yields of 33-43% (Scheme 1). Under these conditions, the reactions of **1a** with more electron-rich arenes, pseudocumene, mesitylene, anisole and veratrole yielded oligomers.




**Scheme 1.** TfOH promoted reactions of **1a** with arenes leading to *gem*-dichloropentenes **2b-d**.

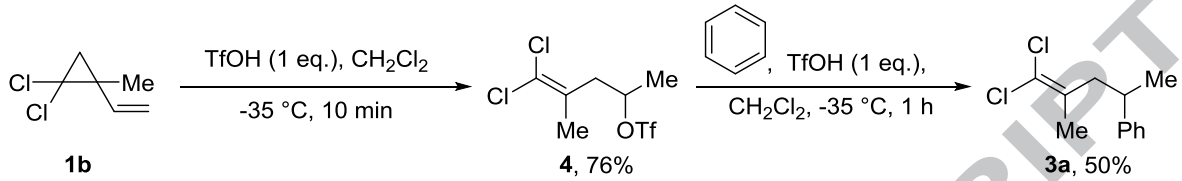
We then studied the transformations of the second vinyl *gem*-dichlorocyclopropane **1b** in TfOH. The reaction of **1b** with benzene took 1 h at -35 °C and gave the product of cyclopropane ring opening **3a** (Scheme 2).




**Scheme 2.** TfOH promoted reaction of **1b** with benzene.

The addition of **1b** to a solution of more electron-rich arenes (isomeric xylenes, pseudocumene) and TfOH in $CH_2Cl_2$ led to oligomers. We then decided to examine the reaction of **1b** using TfOH (1 equiv.) in $CH_2Cl_2$ in the absence of the arene. It was found that, under these conditions at -35 °C, after just 10 min compound **1b** was transformed into triflate **4** in 76% yield (Scheme 3). The reaction of the isolated compound **4** with benzene in $CH_2Cl_2$ in the presence of

TfOH (1 equiv.) at -35 °C for 1 h furnished **3a** (Scheme 3). Compound **4** is unstable and decomposed at room temperature within a few hours. It should be noted, that the reaction of **4** with benzene and other arenes (*vide infra*) did not proceed without TfOH.




**1b** **4**, 76% **3a**, 50%

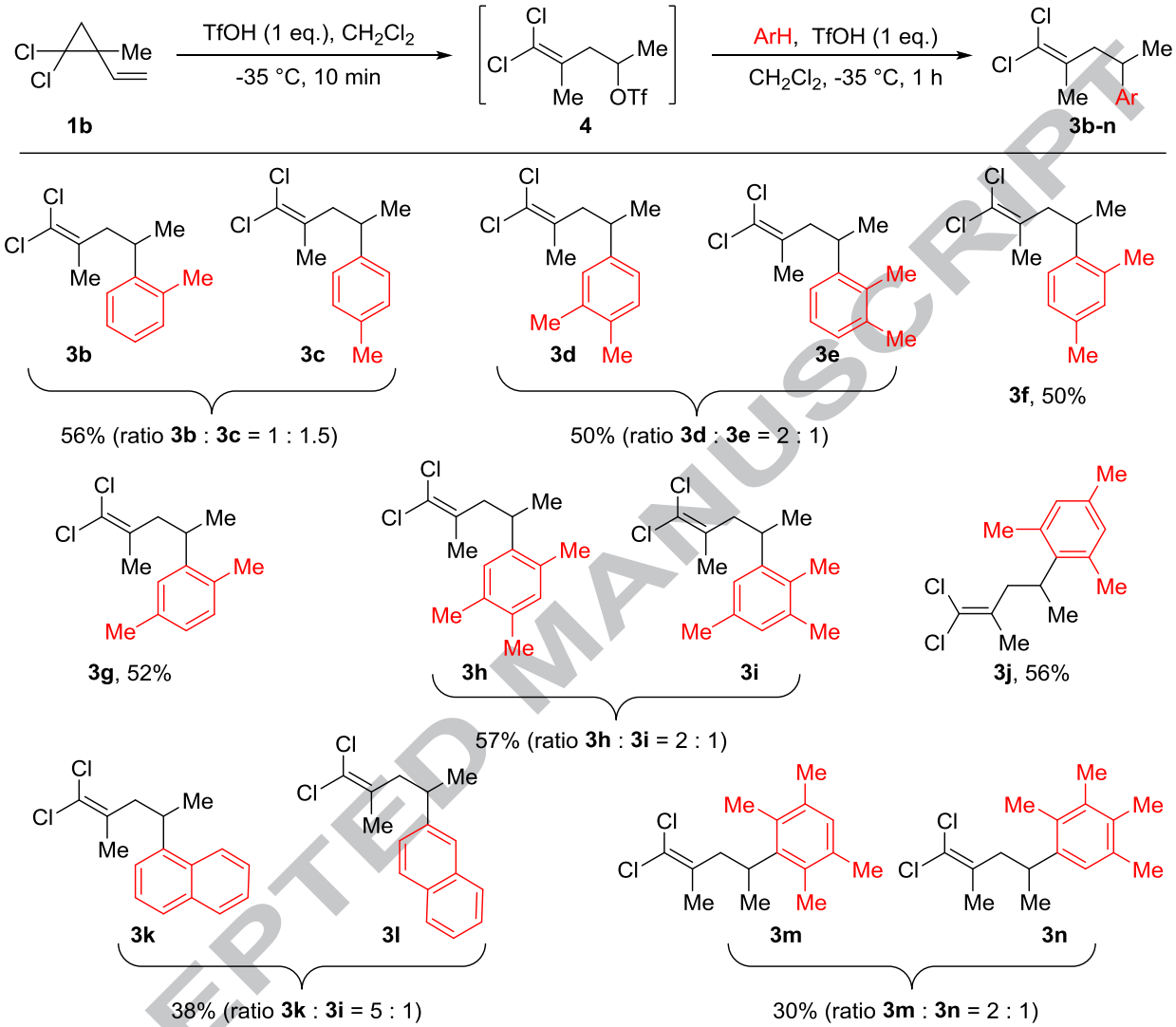
**Scheme 3.** Transformation of **1b** in TfOH leading to triflate **4**, followed by the reaction with benzene resulting in **3a**.

The obtained data revealed that triflate **4** may be the initial reaction product, which is further transformed into **3a** in the reaction with benzene. To check this hypothesis we carried out reactions of **1b** with various arenes *via* the *in situ* generation of intermediate **4** (Scheme 4). Indeed, using this two-step procedure, initial preparation of triflate **4** followed by addition of the arene and a second equivalent of TfOH (ESI, and Scheme 4), resulted in the formation of *gem*-dichloropentenes **3b-n** in 30-57% yield. These compounds were not obtained directly by the addition of **1b** to a solution of arene and TfOH in $CH_2Cl_2$, as mentioned above. In the cases of toluene, *o*-xylene, pseudocumene and naphthalene, mixtures of regioisomers **3b**,**c**, **3d**,**e**, **3h**,**i** and **3k**,**l**, respectively, were obtained. The reaction with durene gave rise to two isomers **3m** and **3n**, with the latter possibly formed as a result of electrophilic attack onto the Cipso-(Me) carbon of the arene ring, followed by the shift of methyl groups on the aromatic ring.

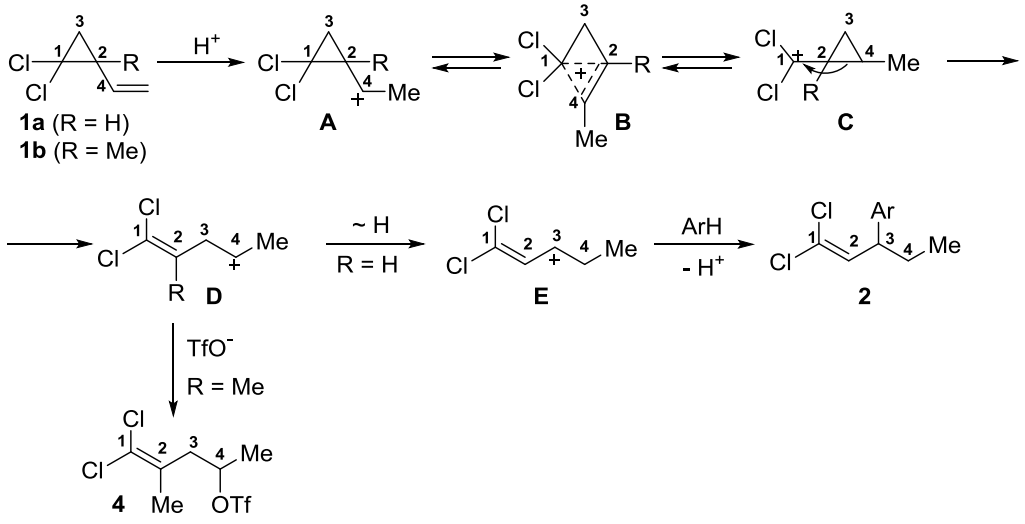
Unfortunately, we failed to obtain a similar triflate in the reaction of **1a** with TfOH; therefore utilization of this two-step procedure could not be used to give the reaction products from the electron-rich arenes, pseudocumene, mesitylene, anisole and veratrole (*vide supra*).

Concerning the reaction mechanism for **1a**,**b**, there are several literature examples of *gem*-dichlorocyclopropane ring opening reactions under the action of Brønsted and Lewis acids.[5,11] Most probably, the reactions start from protonation of the double bond, giving rise to α-cyclopropyl-alkyl cation **A** (Scheme 5). According to the literature[12] the structure of these cation may be represented as non-classical bicyclobutonium ion **B**. In general, there is an equilibrium between several α-cyclopropyl-alkyl cations, such as **A**, **C**, and ion **B**. Finally, ring opening of species **C** leads to homo-allyl cations **D**, which may react in two different ways. The first reaction pathway is realized for **1b** (R = Me) and includes a reaction with the triflate-ion, leading to compound **4**. Upon being isolated and dissolved in TfOH, triflate **4** is transformed to cation **D**. Then the latter reacts with

arenes, yielding compounds **3**. The second reaction pathway (R = H) for species **D** is isomerization into the more stable allyl cation **E**, which reacts with arenes, resulting in compounds **2**.




**Scheme 4.** Reaction of **1b** with arenes leading to *gem*-dichloropentenes **3b-n**.



**Scheme 5.** Plausible mechanism for the TfOH-promoted reaction of **1a**,**b** with arenes.

Of course, this reaction mechanism for **1a,b** is debatable. Despite moderate yields of the target compounds **2** and **3**, the investigated reactions raise interesting questions regarding the detailed mechanisms of these carbocationic transformations and we are currently working on the reactions of other vinyl substituted *gem*-dihalocyclopropanes to better understand these reactions.

In conclusion, the reactions of vinyl substituted *gem*-dichlorocyclopropanes with arenes under the action of the Brønsted superacid TfOH were studied for the first time. The reactions proceed with cyclopropane ring opening and lead to aryl substituted *gem*-dichloropentenes.

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**Supplementary data**

This data contains experimental procedures, characterization of compounds, $^{1}H$, $^{13}C$, $^{19}F$ NMR spectra of compounds.

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Highlights

- Acid-promoted transformations of 1,1-dichloro-2-vinylcyclopropane
- Synthesis of 1,1-dichloropent-1-enes;
- Reaction mechanisms.