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AgOAc-mediated rearrangement of *gem*-dibromospiropentanes in trifluoroacetic acid

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ABSTRACT

AgOAc-mediated intramolecular skeleton rearrangement reaction of *gem*-dibromospiropentanes produced the corresponding naphthalene and indene derivatives in moderate to good yields under mild conditions.

Recently, the chemical transformations and skeleton rearrangements of highly strained oligospirocyclopropanes have attracted much attention from both synthetic and mechanistic viewpoints.[1] Up till now, the chemical transformation of oligospirocyclopropanes can formally be divided into two major sections: (i) reactions with retention of the triangulane skeleton and (ii) reactions accompanied by ring opening or ring enlargement of one or more rings.[2,3] In this Letter, we wish to report a novel example of AgOAc-mediated skeleton rearrangement of easily available *gem*-dibromospiropentanes in trifluoroacetic acid under mild conditions, affording two cyclopropane rings and one cyclopropane ring opened products, naphthalene, and indene derivatives, in moderate to good total yields.[4]

Initial examinations using 2,2-diphenyl-1,1-dibromospiropentane **1a**[5] as the substrate in the presence of AgOAc were aimed at determining the best conditions for this intramolecular skeleton rearrangement reaction and their results are summarized in Table 1. We found that using AgOAc as a mediator, two cyclopropane rings and one cyclopropane ring opened products, naphthalene derivative **2a** and indene derivative **3a**, were formed in 83% total yield with the ratio of 1.28:1 at room temperature (20 °C) (Table 1, entry 1). Examination of the solvent effects revealed that CF_3COOH was the solvent of choice because in dichloromethane, no reaction occurred and in trifluoromethanesulfonic acid CF_3SO_3H (HOTf), complex product mixtures were formed (Table 1, entries 1–3). Raising the reaction temperature to 72 °C, **2a** was obtained as the major product along with only trace of **3a** (Table 1, entry 4). Lowering the temperature to −10 °C, the total yield of **2a** and **3a** could be improved to >99% with the ratio of 1:1.13 (Table 1, entry 5). Using Lewis acids such as $Sc(OTf)_3$, $Yb(OTf)_3$, $Zr(OTf)_4$, $BF_3{\cdot}Et_2O$, or $In(OTf)_3$ as the additive (0.1 equiv), no improvement on the total yield of **2a** and **3a** could be realized whether under reflux, or at room temperature or at −10 °C (Table 1, entries 6–12). We assumed that Lewis acid as the additive might have no effect on the reaction outcomes, and the acidity of the reaction system would play a significant role in this reaction. To prove this, we used the Brønsted acid HOTf as the additive to examine the reaction outcome and found that in higher concentration of HOTf or at higher reaction temperature, **2a** was obtained as the major product, whereas in lower concentration of HOTf or at lower reaction temperature, **2a** and **3a** were usually obtained as the product mixtures in good total yields with different ratios (Table 1, entries 13–17). However, no distinct improvement could be realized if compared with that of the reaction carried out in the absence of HOTf as shown in entry 5 of Table 1. Using strong Brønsted acids $C_8F_{17}SO_3H$ and Tf_2NH, similar results were observed (Table 1, entries 18 and 19). Therefore, the best reaction conditions are to carry out the reaction in CF_3COOH (2.0 mL) at −10 °C using AgOAc (0.30 mmol, 1.5 equiv) as a mediator. Under these optimal conditions, the reaction could complete within 3 h.

With these optimal reaction conditions in hand, we next explored the scope and limitations of this AgOAc-mediated skeleton rearrangement reaction using various *gem*-dibromospiropentanes **1b–k** as the substrates. The results of these examinations are summarized in Table 2. As for the spiropentanes **1b** and **1c** in which both the two aromatic rings had an electron-withdrawing group such as F and Cl atom, the major products were the two cyclopropane rings opened products **2** (Table 2, entries 1 and 2). Moreover, when one of the aromatic rings in spiropentane **1** bore an electron-donating group, such as CH_3 and CH_3O group, one cyclopropane ring opened products **3** were obtained as the major products in good yields (Table 2, entries 3–5). As for spiropentanes **1g–k** in which R^2 is an alkyl group, such as CH_3 or CH_3CH_2 group, the corresponding naphthalene derivatives **2g–k** were mainly obtained in moderate to good yields whether aromatic R^1 group bearing an electron-donating or electron-withdrawing group (Table 2, entries 6–10).

On the basis of the above results, a plausible mechanism of AgOAc-mediated rearrangement reaction is tentatively outlined in Scheme 1.[6] The initial process is more likely to be the generation of spiropentyl cationic intermediate **A** by the elimination of a

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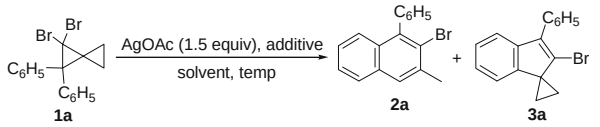
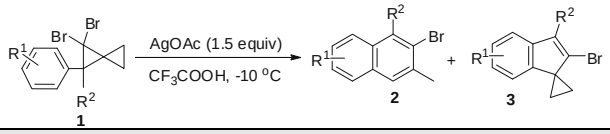
Table 1
Optimization of the reaction conditions[a]



Entry	Additive (mol %)	Solvent	Temperature	Yield[b] (%)	
				2a	**3a**
1	—	CF_3COOH	rt	45	38
2	—	DCM	rt	No reaction	
3	—	HOTf	rt	Complex	
4	—	CF_3COOH	Reflux	52	Trace
5	—	CF_3COOH	−10 °C	47	53
6	$Sc(OTf)_3$(10)	CF_3COOH	Reflux	49	Trace
7	$Yb(OTf)_3$(10)	CF_3COOH	rt	56	32
8	$Zr(OTf)_4$(10)	CF_3COOH	rt	54	35
9	$Sc(OTf)_3$(10)	CF_3COOH	rt	49	42
10	$BF_3{\cdot}Et_2O$(10)	CF_3COOH	rt	53	36
11	$In(OTf)_3$(10)	CF_3COOH	rt	50	36
12	$Yb(OTf)_3$(10)	CF_3COOH	−10 °C	50	50
13	HOTf (100)	CF_3COOH	rt	46	Trace
14	HOTf (50)	CF_3COOH	rt	33	Trace
15	HOTf (20)	CF_3COOH	rt	49	39
16	HOTf (100)	CF_3COOH	−10 °C	61	Trace
17	HOTf (50)	CF_3COOH	−10 °C	44	56
18	$C_8F_{17}SO_3H$ (100)	CF_3CO_2H	−10 °C	46	44
19	Tf_2NH (100)	CF_3CO_2H	−10 °C	58	30

[a] All reactions were carried out using **1a** (0.20 mmol) and AgOAc (0.30 mmol, 1.5 equiv) in solvent (2.0 mL) otherwise specified.
[b] Isolated yields.

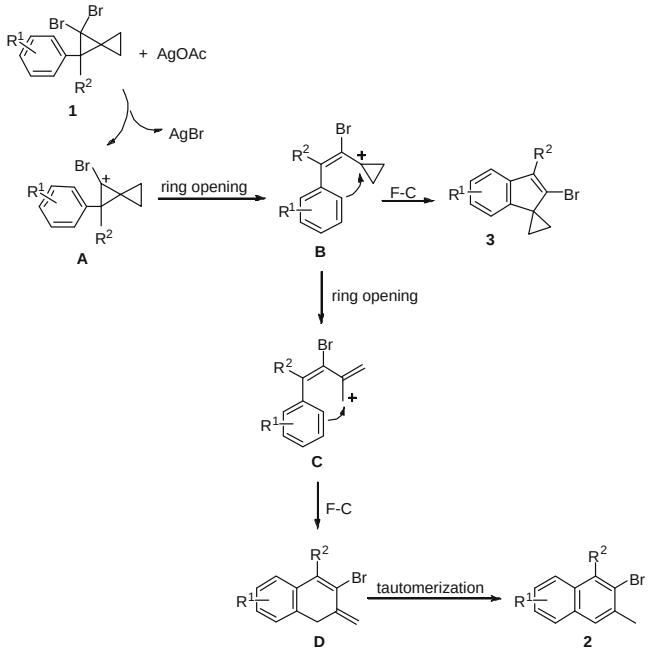
Table 2
AgOAc-mediated skeleton rearrangement of *gem*-dibromospiropentanes 1 under the optimal reaction conditions[a]



Entry	R^1	R^2	No.	Yield[b] of **2** (%)	Yield[b] of **3** (%)
1	*p*-F	*p*-FC_6H_4	**1b**	**2b**, 81	**3b**, 18
2	*p*-Cl	*p*-ClC_6H_4	**1c**	**2c**, 84	**3c**, 10
3	*p*-CH_3O	*p*-$CH_3OC_6H_4$	**1d**	Trace	**3d**, 63
4	*p*-CH_3	*p*-$CH_3C_6H_4$	**1e**	Trace	**3e**, 91
5	H	*p*-$CH_3OC_6H_4$	**1f**	**2f**, 12	**3f**, 60
6	H	CH_3	**1g**	**2g**, 71	Trace
7	H	CH_3CH_2	**1h**	**2h**, 72	Trace
8	*p*-CH_3	CH_3	**1i**	**2i**, 61	Trace
9	*p*-Cl	CH_3	**1j**	**2j**, 95	Trace
10	*m*-Br	CH_3	**1k**	**2k**, 50[c]	Trace

[a] All reactions were carried out using **1** (0.20 mmol) and AgOAc (0.30 mmol, 1.5 equiv) in CF_3COOH (2.0 mL) otherwise specified.
[b] Isolated yields.
[c] The mixture of *o*-and *p*-isomers (1:1) determined by ^1H NMR spectroscopic data.

bromo anion upon the treatment of **1** with AgOAc. The following process might be one of the cyclopropane ring opening reaction to produce the allylic cation **B**, which can directly undergo intramolecular Friedel–Crafts reaction to furnish the corresponding product **3**.[7] In the mean time, intermediate **B** can undergo the ring opening process of another cyclopropane to produce the allylic cation **C**, which is followed by intramolecular Friedel–Crafts reaction to afford intermediate **D**. The tautomerization of intermediate **D** produces the corresponding product **2**. The distribution of products **2** and **3** is mainly dependent on the stability of the two cationic



Scheme 1. A plausible reaction mechanism.

intermediates **B** and **C**. In intermediate **B**, the aromatic ring conjugates to the positively charged allylic moiety, but in intermediate **C**, it is not in such a case. When both the aromatic rings have an electron-withdrawing group, intermediate **B** is not stable and can easily undergo the ring opening process of another cyclopropane to give intermediate **C**. Namely, the formation of intermediate **C** is favored, and the product **2** is the major one. When R^2 is an aliphatic group and R^1 has an electron-donating group, the only one electron-rich aromatic ring is not enough to stabilize the positively charged intermediate **B**, which can still undergo a similar process as mentioned above. However, when both the aromatic rings have an electron-donating group, there exist two electron-rich aromatic rings to stabilize the cationic intermediate **B**. The reaction can mainly proceed directly through intramolecular Friedel–Crafts reaction via intermediate **B** to afford the corresponding indene derivative **3** as the major product.

In conclusion, we have disclosed an interesting AgOAc-mediated skeleton rearrangement reaction of various *gem*-dibromospiropentanes in CF_3COOH to afford the corresponding naphthalene and indene derivatives in moderate to good total yields under mild conditions. Such novel synthetic approach provides an easy access to the synthesis of the interesting naphthalene and indene derivatives, which might be useful in organic synthesis.[8] Efforts are underway to further elucidate the reaction mechanism and to understand the scope and limitations of this process.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.01.116.

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8. *Typical reaction procedure*: *gem*-Dibromospiropentanes **1** (0.20 mmol) and AgOAc (0.30 mmol, 1.5 equiv) were added into a Schlenk tube, and the solvent of CF_3COOH (2.0 mL, prechilled to −10 °C) was added into the mixture of **1** and AgOAc. The reaction mixture was stirred at −10 °C for 2–3 h (monitored by TLC). After the starting materials (*gem*-dibromospiropentanes **1**) were consumed, the solvent was removed under reduced pressure, and the residue was subjected to a flash column chromatography to give the desired product **2** or **3**.Compound **2a**: A yellow solid, mp: 87–89 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.63 (s, 3H, CH_3), 7.24–7.34 (m, 4H, Ar), 7.42–7.55 (m, 4H, Ar), 7.74–7.79 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 24.5, 125.4, 125.8, 126.0, 126.6, 127.1, 127.6, 128.2, 128.3, 130.0, 132.27, 132.29, 135.4, 140.4, 140.5. IR (CH_2Cl_2) ν 3055, 2952, 2922, 2853, 1739, 1440, 1029, 880, 748, 699, 605 cm^{-1}. MS (%) *m/e* 296 (M^+, 37), 215 (55), 202 (58), 189 (12), 108 (32), 85 (40), 71 (60), 57 (100), 43 (94). HRMS (EI) calcd for $C_{17}H_{13}Br$: 296.0201, found: 296.0202.Compound **3a**: A colorless solid, mp: 114–119 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.62–1.66 (m, 2H, CH_2), 1.76–1.80 (m, 2H, CH_2), 7.02–7.05 (m, 1H, Ar), 7.18–7.27 (m, 2H, Ar), 7.38–7.43 (m, 2H, Ar), 7.47–7.52 (m, 2H, Ar), 7.56–7.60 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 16.0, 29.7, 35.2, 117.7, 120.1, 124.7, 125.7, 127.8, 128.4, 128.5, 129.1, 134.2, 139.0, 142.3, 146.5. IR (CH_2Cl_2) ν 3053, 3006, 2925, 1603, 1457, 1345, 965, 769, 746, 699, 661, 619, 574 cm^{-1}. MS (%) *m/e* 296 (M^+, 13), 217 (38), 202 (34), 189 (8), 108 (14), 95 (12), 71 (7), 58 (25), 43 (100). HRMS (EI) calcd for $C_{17}H_{13}Br$: 296.0201, found: 296.0214.