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A New Fluoride-Mediated 1,2-Sulfonyl Shift on Cyclopropane

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Abstract: **A 1,2-sulfonyl shift reaction on cyclopropane proceeded during the reactions of 2-alkynyl-1a-e, 2-aryl-1,1-bis(sulfonyl)cyclopropanes 1f,1j-k and Bu_4NF to give *trans*-1,2-bis(sulfonyl)cyclopropanes 2a-e, 2f, 2j-k.**

The 1,3-rearrangement of a sulfonyl group has been extensively investigated using acid,[1] base,[2] Pd[3] or radical initiators.[4] The 1,5-rearrangement of a sulfonyl group in 1-sulfenylated 2,4-alkadienes is reported to be applicable to a synthetic method for conjugate dienones;[5] however, there are no reports on the 1,2-rearrangement of the sulfonyl group on cyclopropanes because of their highly-strained structures.[6] We now describe a new fluoride-mediated sulfonyl shift reaction on cyclopropanes; a convenient synthesis of 1,2-bis(sulfonyl)cyclopropanes.

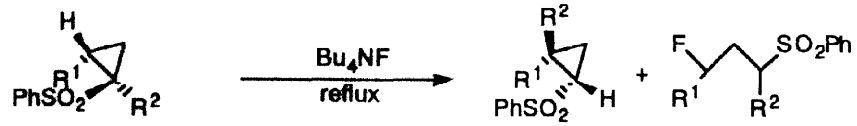

Table 1 1,2-Rearrangement of the Sulfonyl Group on Cyclopropanes

Entry	Cyclopropane			Solvent	Products (%yields)	
		R^1	R^2		rearranged	ring-opened
1	**1a**	Phenylethynyl	$PhSO_2$	THF	**2a** (96)	
2	**1b**	1-Hexynyl	$PhSO_2$	THF	**2b** (60)	
3	**1c**	3,3-Dimethyl-1-butynyl	$PhSO_2$	THF	**2c** (89)	
4	**1d**	3,3-Dimethyl-1-butynyl	Br	THF	**2c** (29)	
5	**1e**	3,3-Dimethyl-1-butynyl	$MeSO_2$	THF	**2e** (86)	
6	**1f**	Ph	$PhSO_2$	THF	**2f** (68)	**3f** (14)
7	**1g**	Et	$PhSO_2$	DME		**3g** (77)
8	**1h**	*t*-Bu	$PhSO_2$	DME		**3h** (85)
9	**1i**	*p*-MeOPh	$PhSO_2$	DME		**3i** (69)
10	**1j**	*p*-Cl-Ph	$PhSO_2$	THF	**2j** (91)	
11	**1k**	*p*-Br-Ph	$PhSO_2$	THF	**2k** (100)	

First, we examined the reaction of 2-(phenylethynyl)-1,1-bis(phenylsulfonyl)cyclopropane (**1a**) and Bu_4NF in THF at 65 °C under an Ar atmosphere. *(1R*,2S*)*-1-(Phenylethynyl)-1,2-bis(phenylsulfonyl)cyclopropane (**2a**) was obtained in 95% yield as a single stereoisomer. The structure was determined by IR, ^1H, ^{13}C NMR, mass spectrum, and elemental analysis. The IR spectrum shows the acetylenic absorption at ν 2230 and the sulfonyl groups at ν 1320 and 1140 cm^{-1}. In the ^1H NMR spectrum, the absorption of the propargyl proton at δ 3.43 ppm disappears and a new absorption of the α-proton of the phenylsulfonyl group at δ 3.63 ppm was observed. The ^{13}C NMR spectrum shows the three carbons of the cyclopropane ring at δ 17.52 (t), 41.72 (s), and 44.07 (d) ppm. The Mass and elemental analysis shows the molecular formula $C_{23}H_{18}O_4S_2$. The new rearrangement was examined using a few bases. *t*-BuOK,

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CH_3CO_2K, $PhSO_2Na$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were found to be ineffective for this reaction. The reaction of **1** with CsF afforded the rearranged product **2a** in 71% yield. These results show that the fluoride anion is effective for this rearrangement reaction. The stereochemistry of the product **2a** was determined by the NOE experiments.[7]

We next examined the reactions of other cyclopropanes with Bu_4NF and these results are shown in Table 1. 2-Alkynyl derivatives **1b,c** also afforded the rearranged products **2b,c** in high yields (Entries 2,3). Bromocyclopropane **1d** did not afford the bromo atom rearranged product; otherwise, the sulfonyl-rearranged product **2c** was obtained in 29% yield (Entry 4). The reaction of *(1R*,2S*)*-2-(3,3-dimethyl-1-butynyl)-1-(methanesulfonyl)cyclopropane (**1e**) gave the rearranged product **2e** as the sole product (Entry 5). The stereochemistry of **2e** was also determined by the NOE experiment.[7] This result shows that the *trans*-methanesulfonyl group against the propargyl hydrogen undergoes a 1,2-rearrangement. The reaction of **1f** and Bu_4NF afforded the rearranged product **2f** in 68% yield; however, the ring-opened by-product **3f** was also obtained in 14% yield (Entry 6). The structure of the ring-opened product **3f** was determined by the ^1H and ^{13}C NMR spectrum. The ^1H NMR spectrum exhibited the benzyl proton at δ 5.85 (ddd, $J_{H\text{-}H}$=4 and 9 Hz, $J_{H\text{-}F}$=48 Hz). The ^{13}C NMR spectrum also exhibited the benzyl carbon at δ 91.60 (d, $J_{C\text{-}F}$=172 Hz) and the methylene carbon at δ 33.46 (d, $J_{C\text{-}F}$=21 Hz). We next performed this reaction with other derivatives **1g** (R=Et) and **1h** (R=*t*-Bu) to give the ring-opened products **3g** and **3h** in high yields (Entries 7 and 8); however, we could not detect the sulfonyl-rearranged products. The *p*-chloro- **1j** and *p*-bromophenyl derivatives **1k** afforded rearranged products **2j** and **2k**, respectively (Entries 10, 11); however, the *p*-MeOPh derivative **1i** predominantly gave the ring-opened **3i** (Entry 9). These results show that the 1,2-rearrangement reactions on the cyclopropanes would contribute to the acidity of the 2-H of these cyclopropanes. The stereoselectivity of the products can be explained as follows. The reaction intermediate would be a sulfonyl-substituted cyclopropene **4**, which is formed from the β-elimination of 1,1-bis(sulfonyl)cyclopropanes. The sulfonyl anion adds to the 2-position of **4** and the resulting cyclopropyl anion **5a** isomerized to the thermodynamically stable intermediate **5b** without the steric hindrance between the sulfonyl groups.[8]

Now we are examining this shift reaction on the cyclopropanes bearing other electron-withdrawing groups and vinylcyclopropane derivatives. These results will be reported elsewhere.

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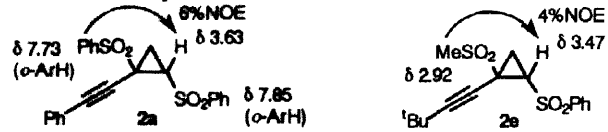
7. The results of the NOE experiments for compounds **2a** and **2e** are shown as follows.



8. The reaction intermediates **4**, **5a** and **5b** are shown as follows.