A Simple and Efficient Conversion of Tertiary Cyclopropanols to 2-Substituted Allyl Halides

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Abstract: Readily available sulphonates of tertiary cyclopropanols are converted into 2-substituted allyl bromides in high yields under the action of magnesium bromide in diethyl ether. Magnesium chloride, aluminium chloride and titanium tetrachloride also induce effectively the transformation of cyclopropyl sulphonates into the corresponding allyl chlorides.

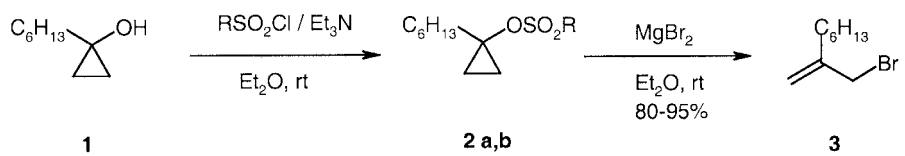
Key words: cyclopropanols, sulphonic esters, ring cleavage, allyl halides, magnesium halides

Tertiary cyclopropanols are readily available by the cyclopropanation of esters,[1,2] desilylation of cyclopropanol silyl ethers,[3,4] alkylation of cyclopropanone hemiacetals,[5,6] and using some other approaches.[7] Their synthetic applications are based mainly on the ring opening reactions, when one of the bonds adjacent to carbinol carbon atom (C1-C2 or C1-C3 bonds in cyclopropane ring) undergoes cleavage. These transformations are usually initiated with electrophilic, basic or oxidizing reagents[4,6–8] and strongly facilitated by electron-donating oxygen atom. In contrast, solvolysis of cyclopropyl *p*-toluenesulphonates and triflates is usually accompanied by the C2-C3 cyclopropane ring cleavage, and these reactions were intensively studied stereochemically and kinetically with a mechanistic interest to the cationic cyclopropyl-allyl rearrangement.[7,9–11] Nevertheless, the preparative value of this transformation was not demonstrated clearly. We now report a simple and highly efficient procedure for the conversion of cyclopropyl sulphonates into 2-substituted allyl halides, which are widely used in organic synthesis, and believe that this finding will contribute to reducing the disbalance in synthetic application of C1-C2 versus C2-C3 modes of the cyclopropanol ring opening reactions.

1-Hexyl-1-cyclopropanol **1** was obtained by the treatment of methyl heptanoate with ethyl magnesium bromide in the presence of titanium(IV) isopropoxide,[1] and was smoothly converted into cyclopropyl sulphonates **2a**,**b** by a standard procedure (Scheme 1).[12] Quite surprisingly, we have found that, in contrast to the solvolysis of cyclopropylsulphonates,[7,10] which proceeded slowly and not unambiguously, the interaction of cyclopropyl mesylate **2a** with magnesium bromide[13] in diethyl ether at room temperature led to allyl bromide **3** in an excellent yield[14] (see Table, entry 1). The reaction of tosylate **2b** with magnesium bromide proceeded at a lower rate, however, the yield of allyl bromide **3** remained high enough (entry 2).

The 1-heptyl (entry 3), 1-phenylmethyl (entry 5), 1-haloalkyl (entries 7–9, 11) and 1-phenyl substituted (entry 12) cyclopropyl sulphonates also gave in this transformation high yields of the corresponding 2-substituted allyl halides. Compounds containing two cyclopropyl sulphonate groups were transformed into the corresponding dienic bromides without any complications (entries 13, 14). Magnesium chloride, as well as aluminium and titanium(IV) chlorides, were also effective in inducing the conversion of cyclopropyl sulphonates into allyl halides (entries 4, 6, 10).

cis-1,2-Disubstituted cyclopropanols (entries 15–19) were prepared by inter-[15] or intramolecular[16] cyclopropanation of the corresponding carboxylic esters with alkylmagnesium halides in the presence of titanium(IV) isopropoxide. In the reaction with magnesium bromide, the respective methanesulphonic esters gave allyl halides as a mixture of stereo- and regioisomers. Compounds with the most substituted double bond were formed preferably in these cases (entries 15–19). The transformation was also successfully applied for the preparation of allyl bromide containing a protected acetal group in the side chain (entry 20).



Scheme 1 R = Me (a), *p*-$CH_3C_6H_4$ (b).

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Table The Reaction of Cyclopropyl Sulphonates with Metal Halides in Diethyl Ether

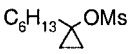
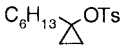
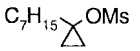
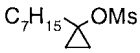
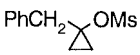
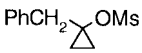
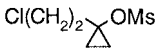
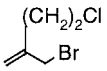
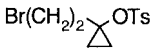
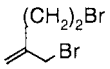
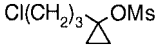
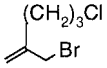
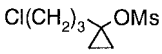
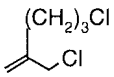
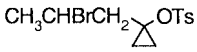
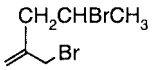
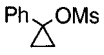
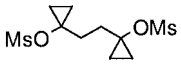
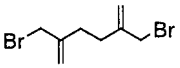
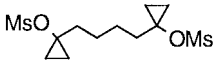
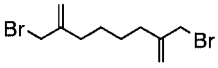
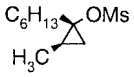
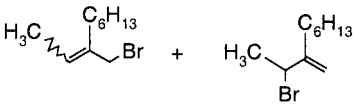
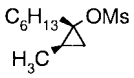
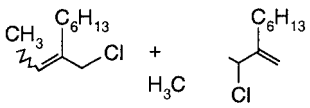
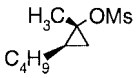
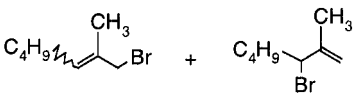
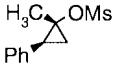
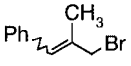
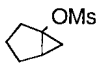
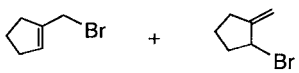
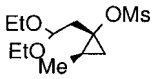
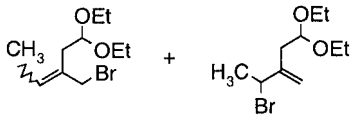
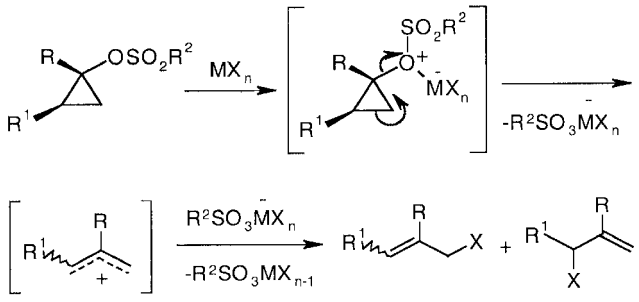
Entry	Cyclopropyl Sulphonate[a]	Metal Halide	Time (h)	Product[b,c]	Isolated Yield, [%]
1	 **2a**	$MgBr_2$	1	 **3**	95
2	 **2b**	$MgBr_2$	12	**3**	80
3		$MgBr_2$	2		90
4		$AlCl_3$	48		80
5		$MgBr_2$	48		68
6		$MgCl_2$[d]	24		72
7		$MgBr_2$	24		70
8		$MgBr_2$	24		81
9		$MgBr_2$	6		71
10		$TiCl_4$	24		79
11		$MgBr_2$	72		79
12		$MgBr_2$	0.5		80
13		$MgBr_2$	3[g]		88
14		$MgBr_2$	5[g]		92
15		$MgBr_2$	2	 65[e]:35	77
16		$TiCl_4$	4	 60[f]:40	62
17		$MgBr_2$	1	 75[g]:25	75
18		$MgBr_2$	1	 100[h]	74
19		$MgBr_2$	1	 90:10	80

Table The Reaction of Cyclopropyl Sulphonates with Metal Halides in Diethyl Ether (continued)

Entry	Cyclopropyl Sulphonate[a]	Metal Halide	Time (h)	Product[b,c]	Isolated Yield, [%]
20		$MgBr_2$	8	 70[i]:30	65

[a] Selected data of substituted methanesulfonates see ref.[17]
[b] Selected data of allyl halides see ref.[18]
[c] *E*/*Z* ratio was determined by ^{1}H NMR spectra.
[d] In dichloromethane.
[e] *E*/*Z* = 90:10.
[f] *E*/*Z* = 70:30.
[g] *E*/*Z* = 85:15.
[h] *E*/*Z* = 85:15.
[i] *E*/*Z* ratio was not determined.

Mechanistically it seems clear, that this reaction includes a Lewis acid assisted heterolytic cleavage of carbon-oxygen bond in cyclopropyl sulphonates which induces a cationic cyclopropyl-allyl rearrangement[7,10] (Scheme 2). The fact that the reaction did not proceed in tetrahydrofuran solution suggests that the Lewis acid should not be excessively solvated. Indeed, cyclopropyl sulphonates reacted faster with magnesium, titanium and aluminium halides in poorly solvating dichloromethane, but formation of allyl halides was sometimes accompanied by resin-like side products.



Scheme 2 R, R^1 = alkyl, aryl; R + R^1 = –$(CH_2)_3$–; R^2 = Me,

In summary, a highly efficient method for conversion of readily available tertiary cyclopropanols to 2-substituted allyl halides have been elaborated.

Acknowledgement

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(11) Momose and co-workers have recently found that treatment of tertiary cyclopropyl silyl ethers with diethylaminosulfur trifluoride give allylic fluorides in moderate to high yield: Kirihara, M.; Kambayashi, T.; Momose, T. *Chem. Commun.* **1996**, 1103.
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(13) We have obtained this finding quite accidentally. A search in the literature revealed that magnesium halides have been earlier proposed by Gore and co-workers as an efficient reagent for nucleophilic displacement of *p*-tosyloxy or mesyloxy groups by halogen atoms: Place, P.; Roumestanant, M.-L.; Gore, J. *Bull. Soc. Chim. Fr.* **1976**, 169.

(14) **Typical Procedure**:
A solution of 1-hexylcyclopropyl methanesulfonate **2a** 7.65 g (35 mmol) in 10 mL Et_2O was added slowly into $MgBr_2$ (52 mmol) solution (prepared from 1.26 g magnesium turnings and 4.5 mL 1,2-dibromoethane in 30 mL Et_2O) at r.t. When the reaction was completed (control by TLC), water was added to the mixture until precipitate was dissolved. Water layer was extracted with Et_2O, washed with 5% NaCl solution and dried over Na_2SO_4. After evaporation of the solvent, the resulting crude product was purified by column chromatography, using petroleum ether eluent and silica gel (Merck 70-230), yielding 6.82 g (95%) of pure allyl halide **3**.

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(17) **Entry 11**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.60–0.74 (m, 1 H), 0.80–0.92 (m, 1 H), 1.06–1.22 (m, 2 H), 1.74 (d, J = 6.5 Hz, 3 H), 2.09 (dd, J_1 = 15 Hz, J_2 = 8 Hz, 1 H), 2.45 (s, 3 H), 2.49 (dd, J_1 = 15 Hz, J_2 = 6 Hz, 1 H), 4.28–4.50 (m, 1 H), 7.35 (d, J = 8 Hz, 2 H), 7.77 (d, J = 8 Hz, 2 H). **Entry 19**: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.92 (t, J = 6 Hz, 1 H), 1.04–1.40 (m, 2 H), 1.58 (dd, J_1 = 12 Hz, J_2 = 8 Hz, 1 H), 1.66–2.06 (m, 3 H), 2.10–2.44 (m, 2 H), 3.02 (s, 3 H).

(18) **Entry 11**: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.76 (d, J = 6.5 Hz, 3 H), 2.61–2.89 (m, 2 H), 4.01 (s, 2 H), 4.17–4.28 (m, 1 H), 5.08 (d, J = 1 Hz, 1 H), 5.32 (s, 1 H). n_D^{20} = 1.5235. **Entry 19:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86–2.06 (m, 2 H), 2.28–2.50 (m, 4 H), 4.08 (s, 1.8 H), 4.88–4.95 (m, 0.1 H), 5.07 (s, 0.1 H), 5.30 (s, 0.1 H), 5.78 (s, 0.9 H).