A Convenient and Stereoselective Method for the Preparation of 2-Substituted 1,3-Alkadienes from 1,2-Disubstituted Cyclopropanols

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Abstract: Sulfonates of *cis*-1,2-disubstituted cyclopropanols are converted into 2-substituted 1,3-alkadienes in moderate to good yields under the action of magnesium perchlorate and triethylamine in diethyl ether. High *trans*-stereoselectivity was observed for the preparation of the alkadienes with a 1,2-disubstituted double bond. The stereochemical outcome in the reaction is consistent with a concerted reaction mechanism involving an $Mg(ClO_4)_2$-initiated cationic cyclopropyl–allyl isomerization of the cyclopropyl sulfonates which is accompanied by a deprotonation.

Key words: cyclopropanols, sulfonates, ring opening, 1,3-dienes, magnesium perchlorate

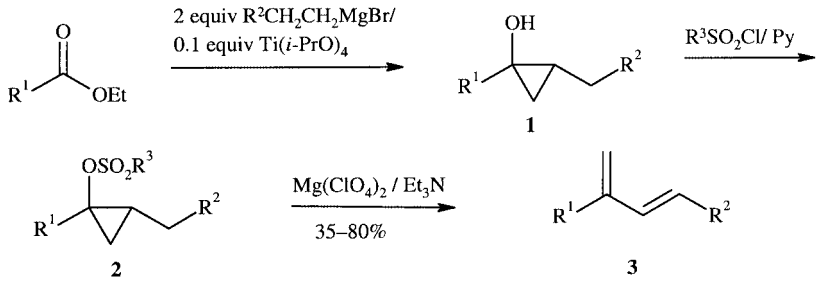
Tertiary cyclopropanols are readily available compounds and their synthetic applications are based mainly on the ring opening reactions, when one of the bonds adjacent to the carbinol carbon atom (C1-C2 or C1-C3 bonds in cyclopropane ring) undergoes cleavage.[1] Recently we disclosed a simple and useful procedure for converting sulfonates of tertiary cyclopropanols into allyl halides under the action of magnesium bromide or some other metal halides in diethyl ether.[2] This reaction includes C2-C3 cyclopropane ring cleavage and proceeds via a cationic cyclopropyl–allyl rearrangement, which is induced by the metal halide assisted heterolytic cleavage of the carbon-oxygen bond in cyclopropyl sulfonates. Transfer of the halide anion from the Lewis acid further captures the allylic cation thus formed.

In this work we have elaborated a convenient method for the transformation of sulfonates of 1,2-disubstituted cyclopropanols into the 2-substituted-1,3-alkadienes, based on the same mode of cyclopropane ring cleavage.

cis-1,2-Disubstituted cyclopropanols **1** were obtained by the treatment of appropriate carboxylic esters with an alkyl magnesium bromide in the presence of titanium(IV) isopropoxide[3,4] and were further smoothly converted into cyclopropyl sulfonates **2** by a standard procedure (Scheme 1).[5] The interaction of mesylate of 1-benzyl-2-methylcyclopropanol (**2a**) with magnesium perchlorate in diethyl ether gave 2-benzyl-1,3-butadiene (**3a**) in 40% yield. The dehydrosulfonation of mesylate **2a** proceeded more effectively in the presence of triethylamine and crude alkadiene **3a** was obtained in 76% yield (see Table 1, entry 1). However, the product contained near 10% impurities (^{1}H NMR). The product could not be separated off by column chromatography on silica gel or alumina.

Alkadiene **3a** was formed in moderate to good yields and could be easy purified by column chromatography when tosylate **2b** was used as substrate (entry 2). The reaction proceeded more clearly and more homogenously in the mixture of diethyl ether and dichloromethane (3:2) as a solvent.

Tosylates of the 1-alkyl and 1-haloalkyl substituted cyclopropanols **2** also gave the corresponding 1,3-alkadienes in moderate to good yields (entries 3–8).



R^1 = alkyl, benzyl, haloalkyl; R^2 = H, alkyl; R^3 = Me, *p*-$CH_3C_6H_4$

Scheme 1

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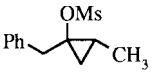
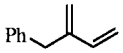
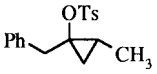
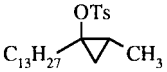
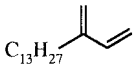
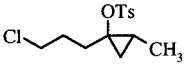
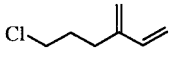
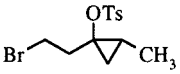
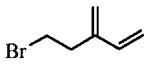
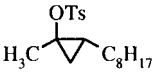
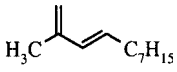
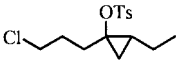
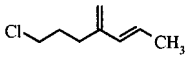
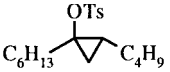
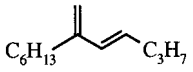
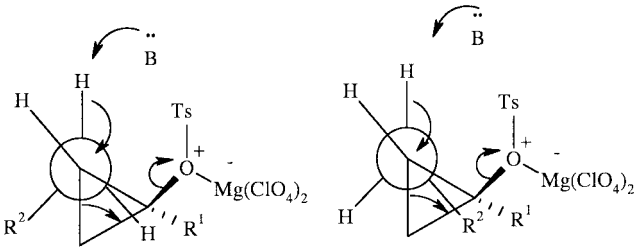
Table 1 Yields of 2-Substituted 1,3-Alkadienes in the Reaction of Cyclopropyl Sulfonates with $Mg(ClO_4)_2$ in the Presence of Et_3N

Entry	Cyclopropyl sulfonate[a,b]	Product[c,d]	Yield (%)[e]
1	 **2a**	 **3a**	76
2	 **2b**	**3a**	70
3			80
4			46
5			45
6			65[f,g]
7			35[f,g]
8			67[f,g]

[a] Typical procedure for the preparation of cyclopropyl sulfonates, see ref.[6,]
[b] Selected data of substituted cyclopropyl sulfonates, see ref.[7,]
[c] Typical procedure for the preparation of 2-substituted 1,3-alkadienes, see ref.[8,]
[d] Selected data of 2-substituted 1,3-alkadienes, see ref.[9,]
[e] Isolated yield after column chromatography on silica gel.
[f] In ^1H NMR spectrum the signals of the corresponding *Z*-isomer were not observed.
[g] The stereochemistry of the 1,2-disubstituted double bond was assigned by the coupling constant of vicinal olefinic protons (J = 15.6 Hz).

High selectivity toward formation of 1,3-alkadienes with *trans*-disubstituted olefinic bonds (entries 6–8) is a remarkable feature of this reaction. We believe that the origin of the observed high *trans*-/*cis*-stereoselectivity arises from a concerted mechanism of the reaction and in this respect there is a formal similarity to the Julia rearrangement of secondary cyclopropyl–carbinyl systems to homoallyl halides.[10] The latter transformation was rationalized by a concerted mechanism of cyclopropane ring opening in the most preferable conformation of the starting cyclopropyl carbinol.[10c] In fact, if concerted mechanism of the dehydrosulfonation of compounds **2** is also realized, the transition states leading to *trans*- and *cis*-isomeric 1,3-alkadienes (entries 6–8) can be depicted by the Newman projection formulas **A** and **B**, respectively (Scheme 2). Non-bonded interactions between hydrogen atoms on the R^1 and R^2 groups in tosylates **2** probably sufficiently destabilize transition state **B** relative to **A**, providing the high *trans*-stereoselectivity of the reaction.



R^1 = alkyl, benzyl, haloalkyl; R^2 = alkyl; B = Et_3N or Et_2O

Scheme 2

In summary, an efficient two-step method for the conversion of readily available tertiary *cis*-1,2-disubstituted cyclopropanols **1** to terminal 2-substituted 1,3-alkadienes **3** has been elaborated. The method is characterized by high *trans*-diastereoselectivity toward formation of the 1,3-alkadienes with disubstituted double bond.

Acknowledgment

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(6) **Typical Procedure:** Tosyl chloride (2.86 g, 15 mmol) was added at once to a solution of 1-benzyl-2-methylcyclopropanol (**1a**, 1.62 g, 10 mmol) in dry pyridine (15 mL) at 0 °C and the mixture was left overnight at r.t. After treatment with ice water (100 mL) and Et_2O (3 × 15 mL), the organic phase was washed with 5% H_2SO_4 (15 mL), aq $NaHCO_3$ (2 × 15 mL) and dried with anhyd Na_2SO_4. After evaporation of the solvents the residue was purified by column chromatography on silica gel (eluent benzene) to give 1.22 g (51%) of tosylate **2b** as a colorless oil.
(7) ^1H NMR (400 MHz, $CDCl_3$): **Entry 2**: δ = 0.47 (t, J = 6.8 Hz, 1 H), 1.16 (d, J = 6.8 Hz, 3 H), 1.35 (dd, J_1 = 10.6 Hz, J_2 = 6.4 Hz, 1 H), 1.52–1.65 (m, 1 H), 2.40 (s, 3 H), 3.05 (d, J = 16 Hz, 1 H), 3.28 (d, J = 16 Hz, 1 H), 7.22 (d, J = 8 Hz, 2 H), 7.30–7.40 (m, 5 H), 7.62 (d, J = 8 Hz, 2 H). **Entry 6**: δ = 0.19 (t, J = 6.4 Hz, 1 H), 0.87 (t, J = 7.2 Hz, 3 H), 1.05–1.40 (m, 16 H), 1.54 (s, 3 H), 2.43 (s, 3 H), 7.31 (d, J = 8 Hz, 2 H), 7.75 (d, J = 8 Hz, 2 H). **Entry 8**: 0.18 (t, J = 6.8 Hz,

1 H), 0.85 (t, *J* = 7.2 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H), 0.98–1.10 (m, 1 H), 1.12–1.55 (m, 19 H), 1.80–1.90 (m, 1 H), 2.43 (s, 3 H), 7.31 (d, *J* = 8 Hz, 2 H), 7.75 (d, *J* = 8 Hz, 2 H).

(8) **Typical Procedure:** A solution of sulfonate **2b** (0.32 g, 1 mmol) in Et_2O (1 mL) was added to a mixture of Et_3N (0.21 mL, 1.5 mmol), $Mg(ClO_4)_2$ (0.67 g, 3 mmol), CH_2Cl_2 (4 mL) and Et_2O (6 mL) at r.t. When the reaction was complete (control by TLC), 2% H_2SO_4 (10 mL) was added to the reaction mixture and the water layer was extracted with Et_2O, the organic layer was washed with sat. $NaHCO_3$ solution (2 × 10 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (eluent petroleum ether), yielding 0.10 g (70%) of diene **3a**.

(9) ^{1}H NMR (400 MHz, $CDCl_3$): **Entry 2**: δ = 3.59 (s, 2 H), 4.94 (s, 1 H), 5.09 (d, *J* = 10.8 Hz, 1 H), 5.20 (s, 1 H), 5.27 (d, *J* = 17.6 Hz, 1 H), 6.47 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1 H), 7.18–7.34 (m, 5 H). **Entry 6**: δ = 0.92 (t, *J* = 6.8 Hz, 3 H), 1.20–1.50 (m, 10 H), 1.87 (s, 3 H), 2.14 (m, *J* = 7 Hz, 2 H), 4.89 (s, 2 H), 5.70 (dt, J_1 = 15.6 Hz, J_2 = 7 Hz, 1 H), 6.17 (d, *J* = 15.6 Hz, 1 H). **Entry 8**: 0.87 (t, *J* = 6.8 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H), 1.25–1.55 (m, 10 H), 2.08 (q, *J* = 7 Hz, 2 H), 2.19 (t, *J* = 7.2 Hz, 2 H), 4.85 (s, 1 H), 4.88 (s, 1 H), 5.68 (dt, J_1 = 15.6 Hz, J_2 = 7 Hz, 1 H), 6.06 (d, *J* = 15.6 Hz, 1 H).

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