Stereochemistry of addition of disulfonium dications to alkenes

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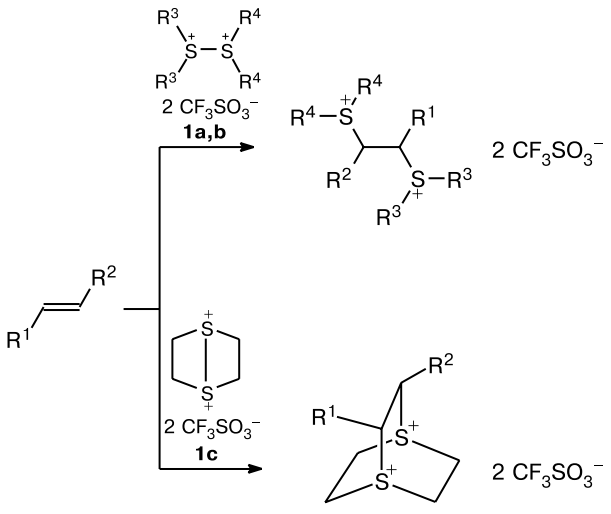
Stereochemistry of the addition of a cyclic disulfonium dication generated from 1,4-dithiane to alkenes was studied. The reaction is nonstereospecific, which can be attributed to a stepwise mechanism.

Key words: sulfonium salts, disulfonium dications, stereochemistry, reaction mechanism, alkenes.

Functionalized sulfonium salts belong to a promising class of electrophilic agents.[1] Disulfonium dications have recently been discovered and attracted particular attention because they possess unique properties due to the presence of two conjugated onium sulfur atoms.[2]

In earlier studies of functionalized sulfonium salts,[3] we have discovered the addition reaction of disulfonium dications at multiple carbon—carbon bonds. It was found that the reactions of disulfonium dications **1a,b** with alkenes afford two diastereomers of the corresponding sulfonium salts[4] (Scheme 1). The reaction of cyclic dication **1c** derived from 1,4-dithiane[5] with a series of activated *trans*-alkenes produces cage bicyclic sulfonium salts of the 1,4-dithioniabicyclo[2.2.2]octane series, the reaction products retaining the relative *trans* configuration of the substituents of the starting alkene[3,6] (see Scheme 1).

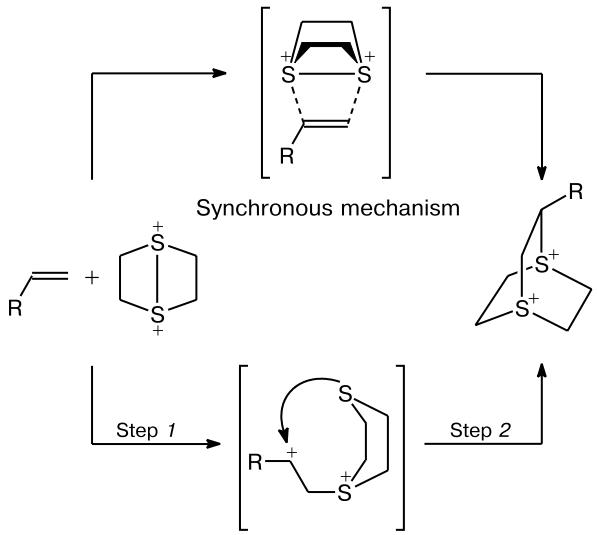
Scheme 1



$R^3 = R^4 = Me$ (**a**); $R^3 + R^3 = R^4 + R^4 = (CH_2)_4$ (**b**)

Based on experimental data on the addition of dication **1c** to alkenes, we have proposed a synchronous mechanism and a stepwise electrophilic mechanism involving carbocationic intermediates[2] (Scheme 2).

Scheme 2



Stepwise electrophilic mechanism

According to the Woodward—Hoffmann rule, the synchronous mechanism involves the formation of a thermally forbidden four-membered transition state, which is highly improbable under the reaction conditions used.[7] The results of quantum-chemical calculations also provided evidence for the stepwise mechanism.[8] However, the formation of only one diastereomer in the reaction of cyclic dication **1c** with alkenes could be a consequence of the synchronous mechanism.

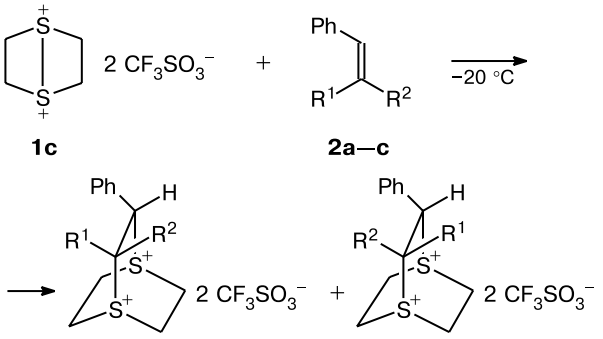
In continuation of the studies on stereochemistry of the reaction, we performed the reactions of diastereo-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1660—1662, August, 2004.

1066-5285/04/5308-1726

merically pure (*de* > 98) (*Z*)-1-phenylpropene (**2a**), (*Z*)-1-phenylbut-1-ene (**2b**), and (*E*)-deuteriostyrene (**2c**) with dication **1c** (Scheme 3). Alkenes **2a,b** were chosen because the assumed intermediates derived from these compounds more readily undergo isomerization compared to those generated from *trans*-alkenes studied earlier. In the case of **2c**, there is no steric hindrance to isomerization of the intermediate due to a small difference in the volumes of hydrogen and deuterium. The reactions of compounds **2a,b** with dication **1c** produced two diastereomers, the major diastereomers containing the substituents of the starting alkenes in a relative *cis* arrangement, whereas the diastereomer with a *trans* arrangement was obtained as the major product in the reaction of **2c**.

Scheme 3



	R^1	R^2	**3** : **4**
a	Me	H	20 : 1
b	Et	H	5 : 1
c	H	D	5 : 1

Unfortunately, bis-sulfonium salts **3** and **4** were prepared in low yields. However, no other identifiable reaction products were isolated.

Since nonstereospecificity of the reaction may be associated with isomerization of the starting alkene under the reaction conditions, we carried out the reactions with an excess of the latter. These experiments demonstrated that the alkene did not undergo isomerization during the reaction.

We also studied the reaction of dication **1c** with alkene **2c** at −20 and 0 °C. If the reaction proceeds by a stepwise mechanism and the diastereomer ratio is determined by the difference in the rates of isomerization and ring closure in the intermediate carbocation, the change in the temperature would change the rates of both processes and, as a consequence, the diastereomer ratio. Actually, an increase in the temperature from −20 to 0 °C resulted in the formation of the only diastereomer with a relative *trans* arrangement of the substituents in the bridge.

Hence, the results of our study demonstrate that the reaction of cyclic dication **1c** with alkenes **2a—c** proceeds nonstereospecifically. This is further proof of the fact that the reaction occurs by a stepwise mechanism.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz) in $CDCl_3$ and CD_3CN with Me_4Si as the internal standard. The TLC analysis was carried out on Silufol UV-254 plates, visualization was performed with an acidified solution of $KMnO_4$ and iodine vapor.

The solvents were dried according to conventional procedures: CH_2Cl_2 by distillation from P_2O_5, and Et_2O by distillation from Na in the presence of benzophenone.

The starting (*Z*)-1-phenylpropene (**2a**) and (*Z*)-1-phenylbut-1-ene (**2b**) were synthesized from 1-phenylpropyne and 1-phenylbut-1-yne, respectively, according to a known procedure.[9] (*E*)-Deuteriostyrene (**2c**) was prepared from *trans*-ω-bromostyrene.[10]

Reaction of dication 1c with alkenes 2a—c (general procedure). A solution of 1,4-dithiane (0.6 g, 5 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to a solution of $(CF_3SO_2)_2O$ (1.7 g, 6 mmol) in anhydrous CH_2Cl_2 (20 mL) at −40 °C. The reaction mixture was stirred at −20 °C for 15 min. Then a solution of the substrate (5 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise, the mixture was kept at −20 °C for 3—12 h (TLC control), and an equal amount of anhydrous diethyl ether was added. The precipitate of the bis-sulfonium salt that formed was filtered off, washed three times with anhydrous diethyl ether, and dried *in vacuo*.

The diastereomer ratio of bis-sulfonium salts **3** and **4** was determined by comparing the intensities of the characteristic signals for the protons at the C(2) atom at δ 5.5—5.7. The relative configuration of the diastereomers was determined from the coupling constants of the protons at the C(2) and C(3) atoms.[4]

2-Methyl-3-phenyl-1,4-dithioniabicyclo[2.2.2]octane bis(trifluoromethanesulfonate) (3a + 4a). The yield was 20%, m.p. 110—113 °C (with decomp.). Found (%): C, 33.42; H, 3.54. $C_{15}H_{18}F_6O_6S_4$. Calculated (%): C, 33.58; H, 3.38. IR, ν/cm^{-1}: 1260—1170 (CF_3); 1035 (SO_3). ^{1}H NMR of the major isomer (CD_3CN), δ: 1.37 (d, 3 H, Me, J = 7.7 Hz); 3.87—4.28 (m, 8 H, CH_2); 4.77 (dq, 1 H, C(2)H, J = 9.2 Hz, J = 7.7 Hz); 5.59 (d, 1 H, C(3)H, J = 9.4 Hz); 7.44—7.58 (m, 5 H, Ph). ^{13}C NMR of the major isomer (CD_3CN), δ: 14.18 (Me); 20.61, 24.83, 27.60, 30.55 (C(8), C(7), C(6), C(5)); 40.74 (C(3)); 47.36 (C(2)); 121.84 (q, 2 CF_3, $J_{C,F}$ = 320.56 Hz); 129.49 (C(2′), C(6′)); 129.58 (C(1′)); 130.77 (C(3′), C(5′)); 131.58 (C(4′)).

2-Ethyl-3-phenyl-1,4-dithioniabicyclo[2.2.2]octane bis(trifluoromethanesulfonate) (3b + 4b). The yield was 20%, m.p. 167—169 °C (with decomp.). Found (%): C, 34.69; H, 3.80. $C_{16}H_{20}F_6O_6S_4$. Calculated (%): C, 34.90; H, 3.66. IR, ν/cm^{-1}: 1260—1170 (CF_3); 1035 (SO_3). ^{1}H NMR of the major isomer (CD_3CN), δ: 0.94 (t, 3 H, $CH_2C\underline{H}_3$, J = 8.0 Hz); 1.57—1.73 (m, 2 H, $C\underline{H}_2CH_3$); 3.88—4.28 (m, 8 H, CH_2); 4.59 (dt, 1 H, C(2)H, J = 9.7 Hz, J = 7.5 Hz); 5.62 (d, 1 H, C(3)H, J = 9.7 Hz); 7.44—7.61 (m, 5 H, Ph). ^{13}C NMR of the major isomer (CD_3CN), δ: 14.18 ($CH_2\underline{C}H_3$); 22.61 ($\underline{C}H_2CH_3$); 21.02, 24.89, 27.12, 30.41 (C(8), C(7), C(6), C(5)); 40.61 (C(3)); 47.74 (C(2)); 119.99 (q, 2 CF_3, $J_{C,F}$ = 320.57 Hz); 129.88 (C(2′), C(6′)); 130.17 (C(1′)); 130.81 (C(3′), C(5′)); 131.72 (C(4′)).

[3-^{2}H]-2-Phenyl-1,4-dithioniabicyclo[2.2.2]octane bis(trifluoromethanesulfonate) (3c + 4c). The yield was 44%, m.p. 120—122 °C (with decomp.). IR, ν/cm^{-1}: 1260—1170 (CF_3); 1035 (SO_3). ^{1}H NMR of the major isomer (CD_3CN), δ: 3.69—4.16 (m, 8 H, CH_2); 4.34 (td, 1 H, C(2)H, J = 9.7 Hz, $J_{H,D}$ = 2.8 Hz); 5.49 (d, 1 H, C(3)H, J = 9.7 Hz); 7.57—7.71 (m, 5 H, Ph). ^{13}C NMR of the major isomer (CD_3CN), δ: 24.18, 25.34, 25.46, 29.05 (C(8), C(7), C(6), C(5)); 29.71 (t, C(3), $J_{C,D}$ = 22.69 Hz); 45.11 (C(2)); 121.91 (q, 2 CF_3, $J_{C,F}$ = 322.03 Hz); 129.87 (C(2′), C(6′)); 130.04 (C(1′)); 131.05 (C(3′), C(5′)); 132.37 (C(4′)).

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32024-a).

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Received January 27, 2004