Intramolecular Transfer of Sulfonyl Oxygen to Vinylcarbene Generated in the Reaction of Tris(isopropylthio)cyclopropenyl Cation with Arylsulfinate Salts

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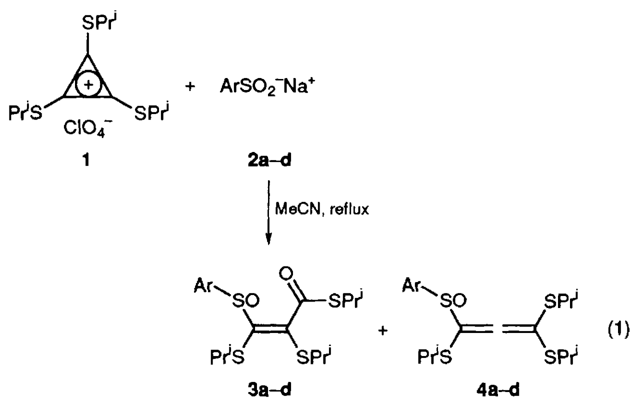
Tris(isopropylthio)cyclopropenylium perchlorate **1** reacts with sodium arylsulfinates **2a–d** in dry acetonitrile and benzene under reflux to give arylsulfinylpropenethioates **3a–d**, accompanied by the formation of arylsulfonylallenes **4a–d**, through cyclopropene intermediates **5a–d** and then vinylcarbenes **6a–d**.

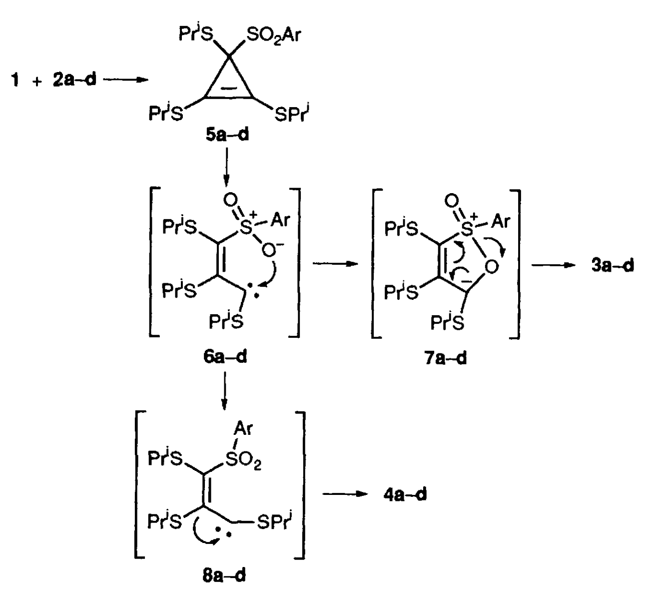
Tris(isopropylthio)cyclopropenylium perchlorate **1** is a useful three-carbon building block in synthetic reactions, as it reacts smoothly with nucleophiles to give vinylcarbene intermediates by ring opening. Recently, we have reported the synthesis of nitrogen heterocycles in high yields by the intramolecular cyclization of the pyridinoid nitrogen to the carbenic carbon in the preparation of indolizine and pyrroloazole derivatives from 2-pyridylmagnesium bromide[1] and 2-lithioazoles,[2] respectively. On the basis of this study, we considered that vinylcarbenes, generated from **1** and arylsulfinate salts, could undergo cyclization with the sulfonyl oxygen. We carried out the reaction of **1** with sodium derivatives of toluene-*p*-, benzene-, 4-methoxybenzene- and 4-chlorobenzene-sulfinates **2a-d** and now report the first example of the intramolecular transfer of the sulfonyl oxygen to the carbenic carbon to give arylsulfinylpropenethioates **3a-d** [*e.g.* eqn. (1)]. This oxygen-



a; Ar = 4-MeC$_6$H$_4$
b; Ar = Ph
c; Ar = 4-MeOC$_6$H$_4$
d; Ar = 4-ClC$_6$H$_4$

transfer reaction is of interest in relation to the deoxygenation of sulfones *via* the reaction of aryloxysulfonium salts, derived from sulfones, with hydrides[3] and nucleophiles.[4]

The reaction of **1** with 2 equiv. of sodium toluene-*p*-sulfinate **2a** was carried out under nitrogen in dry MeCN under reflux for 1 h. Workup with dichloromethane extraction and subsequent chromatography on silica gel eluting with hexane–dichloromethane (2 : 1) gave *S*-isopropyl-2,3-bis(isopropylthio)-3-tolylsulfinylpropenethioate **3a** in 64% yield. In this rection, 1,1,3-tris(isopropylthio)-3-tosylpropadiene **4a** was obtained as a byproduct in 35% yield. Furthermore, it was confirmed that 1,2,3-tris(isopropylthio)-3-tosylcyclopropene **5a**,† prepared from **1** and **2a** in dry MeCN at room temperature, is converted into **3a** and **4a** in 64 and 35% yields, respectively, on refluxing **5a** in dry MeCN for 1 h. The structures of **3a** and **4a** were established by ^{1}H and ^{13}C NMR and IR spectroscopy. The IR spectrum of **3a** showed a signal due to the S=O stretching at 1050 cm^{-1} and a signal due to the C=O stretching at 1660 cm^{-1}. The ^{13}C NMR spectrum of **3a** showed a signal for the carbonyl carbon at δ 190.7. The stereochemistry for **3a** was specified by NOE experiments.† The allenic structure of **4a** was established by IR spectroscopy, which showed a signal due to the C=C=C stretching at 1910 cm^{-1}. The reaction of **1** with **2b–d** also gave arylsulfinylpropenethioates **3b–d** in 61, 59 and 60% yields together with arylsulfonylallenes **4b–d** in 38, 40 and 39% yields, respectively. The structures of **3b–d** and **4b–d**† were determined similarly as for **3a** and **4a**; the yields of **3a–d** and **4a–d** were little influenced by the nature of the substituents in the *p*-position. Furthermore, it was revealed that the product ratio does not vary with different cations: the reaction of **1** with lithium, potassium and tetrabutylammonium toluene-*p*-sulfinates under similar conditions gave **3a** in 67, 66 and 65% yields and **4a** in 25, 33 and 34% yields, respectively.



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Scheme 1

Table 1 Solvent effects on the yields of **3a** and **4a**[a]

Solvent	*T*/°C	Yield (%)[b] **3a**	**4a**
N,N-Dimethylformamide	80	70	29
Chloroform	Reflux	77	22
Tetrahydrofuran	Reflux	84	15
Benzene	Reflux	90	9
Toluene	80	90	9

[a] Molar ratio of **1** : **2a** = 1 : 2. [b] Isolated yields based on **1**.

To investigate the solvent effects on the product ratios, the reaction of **1** with **2a** was carried out in various solvents, heating for 1 h. In all cases, the reaction gave **3a** and **4a** in quantitative yields, as shown in Table 1. The yield of **3a** was found to increase with decreasing the solvent polarity. In nonpolar solvents such as benzene and toluene, the disperse solution became homogeneous as the reaction proceeded, and the yield of **3a** reached 90%. Cyclopropene **5a** also was converted into **3a** and **4a** in 90 and 9% yields, respectively, by refluxing **5a** in dry benzene.

The reaction pathway for the formation of **3a–d** can be explained by the formation of the vinylcarbene intermediates **6a–d** by ring opening of cyclopropenes **5a–d**, followed by the intramolecular transfer of the sulfonyl oxygen of **6a–d** to the carbenic carbons through the formation of **7a–d** by cyclization, as shown in Scheme 1. On the other hand, **4a–d** are considered to be produced by the rearrangement of the isopropylthio group to the carbenic carbon of the rotational isomers **8a–d**.

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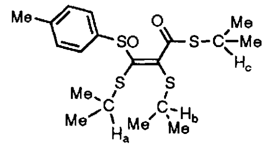
† Compounds **3a–d**, **4a–d** and **5a** gave satisfactory ^{1}H and ^{13}C NMR and IR spectroscopic data and elemental analyses.

Selected data: **3a**: ^{1}H NMR (CDCl$_3$) δ 1.16 (3 H, d, *J* 6.7 Hz), 1.22 (3 H, d, *J* 6.7 Hz), 1.31 (3 H, d, *J* 6.7 Hz), 1.35 (3 H, d, *J* 6.7 Hz), 1.44 (6 H, d, *J* 6.7 Hz), 2.38 (3 H, s), 3.46 (1 H, sep, *J* 6.7 Hz), 3.62 (1 H, sep, *J* 6.7 Hz), 3.85 (1 H, sep, *J* 6.7 Hz), 7.27 (2 H, d, *J* 7.0 Hz) and 7.60 (2 H, d, *J* 7.0 Hz); ^{13}C NMR (CDCl$_3$) δ 21.5, 22.6, 22.7, 22.9, 23.5, 24.6, 36.8, 38.1, 39.4, 125.4, 129.6, 139.1, 141.1, 142.3, 153.4 and 190.7; IR ν/cm^{-1} (KBr) 1660 (C=O) and 1050 (S=O).

4a: ^{1}H NMR (CDCl$_3$) δ 1.22 (6 H, d, *J* 6.7 Hz), 1.33 (6 H, d, *J* 6.7 Hz), 1.35 (6 H, d, *J* 6.7 Hz), 2.45 (3 H, s), 3.18 (1 H, sep, *J* 6.7 Hz), 3.25 (2 H, sep, *J* 6.7 Hz), 7.34 (2 H, d, *J* 7.9 Hz) and 7.83 (2 H, d, *J* 7.9 Hz); ^{13}C NMR (CDCl$_3$) δ 21.7, 22.8, 23.2, 23.4, 39.2, 39.7, 111.9, 112.5, 128.7, 129.9, 136.7, 144.7 and 203.0; IR ν/cm^{-1} (neat) 1910 (C=C=C).

5a: ^{1}H NMR (CDCl$_3$) δ 1.17 (6 H, d *J* 6.7 Hz), 1.40 (6 H, d, *J* 6.7 Hz), 1.43 (6 H, d, *J* 6.7 Hz), 2.43 (3 H, s), 3.18 (1 H, sep, *J* 6.7 Hz), 3.45 (2 H, sep, *J* 6.7 Hz), 7.32 (2 H, d, *J* 7.9 Hz) and 7.85 (2 H, d, *J* 7.9 Hz); IR ν/cm^{-1} (neat) 1300 (SO$_2$) and 1145 (SO$_2$).

Difference NOE of **3a**: upon irradiation of H$_a$ at δ 3.62 an NOE was observed for H$_b$ at δ 3.46, whereas upon irradiation of H$_c$ at δ 3.85 an NOE was observed for H$_b$.



The solvation of **6a–d** by a polar solvent may interfere with the formation of **7a–d**, thus lowering the yields of **3a–d**.

The above results provide evidence for the intramolecular deoxygenation of the sulfonyl oxygen by vinylcarbene in the reactions of **1** with **2a–d**.

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