

Nucleophilic Reactivity of Sulfonyl Oxygen. Detection and Isolation of γ -Sultinium Ions†

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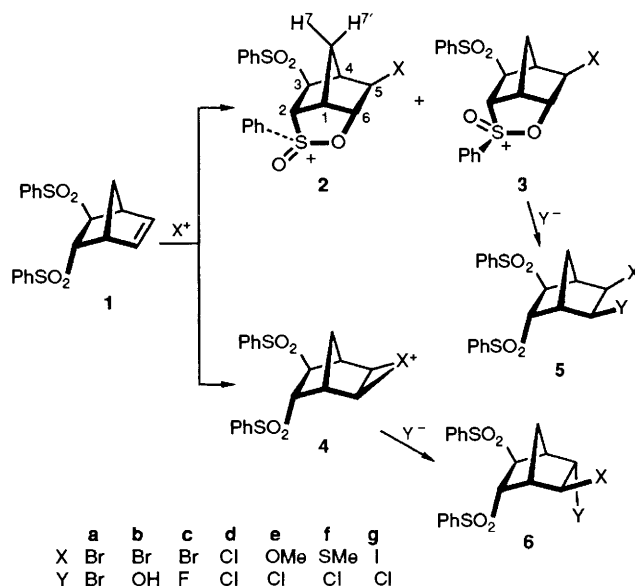
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The addition of Cl₂, Br₂ or ICl to 2-*endo*-3-*exo*-bis(phenylsulfonyl)norborn-5-ene **1** in the presence of AgBF₄, or the methylation of the epoxide of **1** allow the observation or isolation of the isomeric γ -sultinium ions **2** and **3** (X = Cl, Br, I, OMe); the addition of Me₃S₃⁺SbCl₆⁻ leads to thiiranium ion **4** (X = SMe); in the case of X = I, **2** and **3** interconvert *via* the intermediacy of **4**.

Sulfonyl oxygens are rather weak bases¹ and poor nucleophiles. Only one report has appeared, describing the nucleophilic attack to very reactive arenium ions, with the formation of aryloxysulfoxonium salts.² The intramolecular nucleophilic reactivity has been reported more frequently, both in the case of the synthesis of sultines³ and in the case of neighbouring group participation during electrophilic additions.⁴ The intermediate for intramolecular nucleophilic attack, the sultinium ion, has been observed so far only in one particular situation of reagent proximity and molecular rigidity.^{4b} We found that sultinium ions are remarkably stable molecules which can be easily generated from a variety of substrates, using the simple procedures described here.

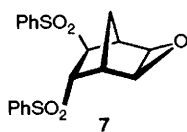
The addition of Br₂ to an equimolar solution of 2-*endo*-3-*exo*-bis(phenylsulfonyl)norborn-5-ene **1**⁵ and AgBF₄ in CH₂Cl₂ affords, after filtration from AgBr and precipitation with pentane, a hygroscopic white powder. The ¹H NMR spectrum of this substance in CD₂Cl₂ points to the presence of two compounds.‡ The almost complete networks of NOE

dipolar interactions,⁶ measured with NMR differential spectroscopy, are consistent with the two epimeric γ -sultinium ions **2a** and **3a**. Two doublets at δ 6.38 and 6.22, in the 40 : 60 ratio,



† The name sultine is used to describe a cyclic sulfinate ester and is analogous to a sultone with an -SO-O- rather than an -SO₂-O- linkage.

‡ The cationic intermediates were characterized by ¹H NMR spectra; the final adducts also by combustion analyses and mass spectra.



give significant NOE interactions with signals belonging to one methane bridge proton, and should, therefore, be assigned to the strongly deshielded *endo* alkyl protons H⁶. In the minor isomer, the *ortho* protons of sultinium phenyl interact with vicinal H² and also with the bridgehead H¹, thus allowing the assignment of the stereo structure **3a**. In the major isomer, with structure **2a**, the interaction is with vicinal H² and with H³, geminal to the free sulfonyl group. The salts **2a** and **3a** are relatively stable in solution: they react in about 3 days at room temperature with adventitious water or BF₄⁻ (or with F⁻ generated by hydrolysis), leading to the *exo-syn* adducts **5b** and **5c** (structural determinations by NOE).

When Br₂ is added to **1** in liquid SO₂, two doublets are observed in the δ 6.2–6.5 region, diagnostic for the presence of **2a** and **3a**.§ Their signals are replaced, in about 10 min at room temperature, by those of the *exo-syn* adduct **5a**.^{4d} On the other hand, when the addition is carried out in CH₂Cl₂, **5a** is formed instantly.

In the same manner, the resonance of **2d** and **3d** are transiently observed when **1** is added to a solution of Cl₂ in liquid SO₂. Again, in about 15 min, they give place to those of the *exo-syn* adduct **6d**.

Finally, the resonances diagnostic for **2e** and **3e** are observed when the epoxide **7**^{4d} is methylated with Me₃O⁺BF₄⁻ in CD₂Cl₂. The addition of Cl⁻ (from *N*-methylpyridinium chloride) yields the *exo-syn* compound **5e**.

The reaction of **1** with methanesulfonyl chloride takes a different course, giving the *anti* adduct **6f**. This stereochemistry implies the intermediacy of the corresponding thiiranium ion **4f**. We could indeed easily generate and isolate the hexachloroantimonate salt of **4f**, by reacting **1** with (MeS)₂MeS⁺ SbCl₆⁻⁷ in SO₂ or CD₂Cl₂. The structure was unambiguously determined through NOE experiments; particularly diagnostic was the detection of relevant interactions among the three *endo* protons. The addition of Cl⁻ (from *N*-methylpyridinium chloride) gives the expected *anti* adduct **6f**.

The addition of ICl seems to be a borderline case. In SO₂ very broad resonances are observed at room temperature, which in about 30 min transform into sharp signals of both *exo-syn* and *anti* adducts **5g** and **6g**, in a 70 : 30 ratio (structural determination by NOE). When the reaction is immediately monitored at –60 °C, the 'frozen' resonances of sultinium ions **2g** and **3g** are observed, while those of the putative iodiranium ion **4g** are below the instrumental detection limit. By raising the temperature the **2g** : **3g** ratio changes (as monitored in the δ 6.2–6.5 region); at about 0 °C an incipient broadening is observed, while the resonances of the final adducts **5g** and **6g** appear. The ratio change is indicative of an easy interconversion between sultinium ions **2g** and **3g**, which must occur *via* the intermediacy of iodiranium ion **4g**. At room temperature the interconversion rate is comparable with the NMR frequency scale. Although not observed, a significant amount of

the iodiranium ion should be present. At the same time, the fact that the equilibrium is almost totally shifted toward the sultinium ion side signifies that iodiranium iodine is a much better nucleofuge than sultinium oxygen. It is then plausible that Cl⁻ attack to the more electrophilic iodiranium ion **4g** may generate the *anti* adduct **6a** in an amount comparable to that of the *exo-syn* adduct **5a**.

The stability of sultinium ions **2** and **3** should be modestly affected by the nature of the X substituent. Therefore, they may represent a reliable reference for the stability of the different iranium ions. Our investigation gives the stability scale SR >> I > Br, Cl, OR. This is in line with the stability scales (SR > OR and I > Br > Cl) deduced from quantum mechanics calculations,⁸ solvolysis reactions with halogen anchimeric assistance,⁹ observation and isolation of iranium ions.¹⁰

Finally, the stability of the cationic intermediates **2**, **3** and **4**, under the described reaction conditions, offer the possibility of a wider choice for the final nucleophile.

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