The First Successful Polar Cycloaddition of 1-Benzothiopyranylium Salts with Conjugated Dienes and Transformation of the Cycloadducts

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1-Benzothiopyranylium salts **1** underwent polar cycloaddition with conjugated dienes **2** to give benzo-fused bicyclic sulfonium salts **3** having sulfur at a bridgehead position in good yields, which were easily transformed into spiro compounds **4** and **5** by treatment with base.

We recently reported the first successful cycloaddition of 2-benzothiopyranylium salts (thiopyrylium derivatives) with 1,3-dienes giving benzo-fused bicyclic sulfonium salts as isolable compounds.[1] In our continuing studies on the polar cycloaddition of thiopyrylium derivatives, we are interested in the reactivity of 1-benzothiopyranylium salts **1** which behave either as electron-deficient dienes or as dienophiles in cycloadditions, because their canonical structures include both α- and γ-thiocarbocations. We have now succeeded in the [2+ + 4] cycloaddition of the salts **1** with conjugated dienes and found an interesting ring transformation of the cycloadducts caused by base.

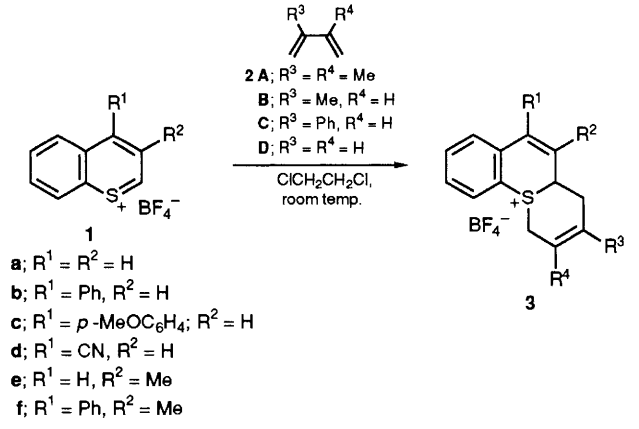
Treatment of the parent tetrafluoroborate **1a** with 2,3-dimethylbuta-1,3-diene **2A** (2 mol. equiv.) in dry dichloroethane at room temperature for 30 min afforded the cycloadduct **3aA** in 70% yield, showing that the ion **1** behaves as a dienophile, but not as an electron-deficient diene. To our knowledge, this is the first reported example of a polar cycloaddition of a 1-benzothiopyranylium ion with a 1,3-diene. Cycloaddition of isoprene **2B** with **1a** proceeded regiospecifically to afford the cycloadduct **3aB** as a single regioisomer in 66% yield.† The regiostructure of the cycloadduct **3aB** was determined mainly by ^{1}H NMR spectroscopy.

In order to investigate the possible electronic and steric influences of substituents on the hetero ring, we studied the cycloaddition of a variety of 3- and/or 4-substituted 1-benzothiopyranylium salts with 1,3-dienes. The results are summarized in Table 1. The yields of the cycloadducts of 4-aryl derivatives **1b, c, f** were better than that of the 4-unsubstituted compound. The 4-cyano compound **1d** activated with an electron-withdrawing group reacted more rapidly with 1,3-dienes to give the corresponding cycloadducts in excellent yields (entries 6–8). A 3-methyl group tends to decrease the reaction rate and the yield of cycloadducts, probably because of steric interference to the attack of the 1,3-diene on the thiopyrylium ion (entries 10–12). Reaction with isoprene **2B**

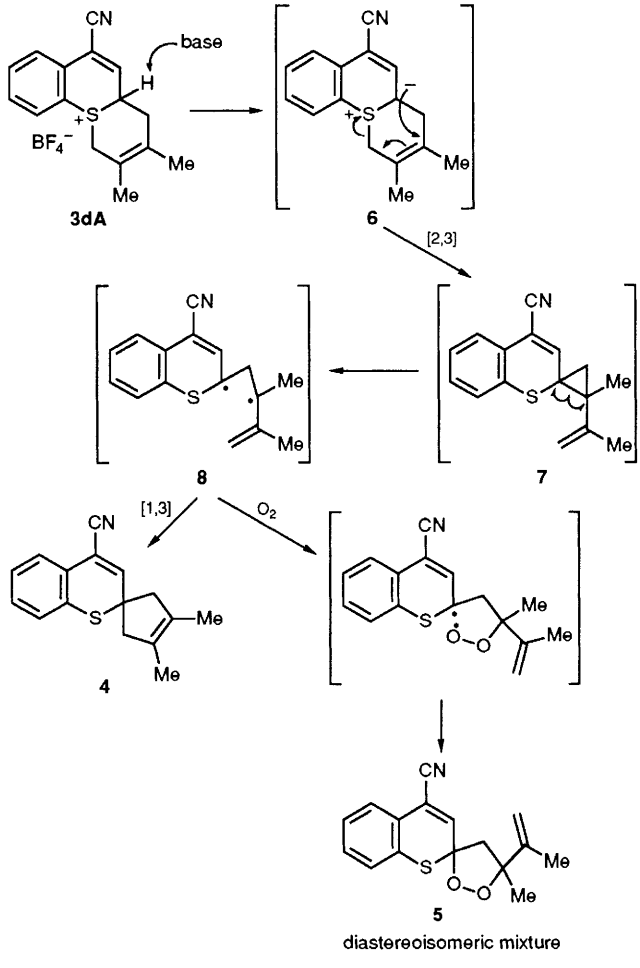
Table 1 Polar cycloadditions of 1-benzothiopyranylium salts **1** with 1,3-dienes **2**

	Reactants			Product	
Entry	Salt	Diene	*t*/min	Compd.	Yield (%)
1	**1a**	**2A**	30	**3aA**	70
2	**1a**	**2B**	30	**3aB**	66
3	**1b**	**2A**	20	**3bA**	89
4	**1b**	**2B**	20	**3bB**	66
5	**1c**	**2A**	20	**3cA**	87
6	**1d**	**2A**	5	**3dA**	94
7	**1d**	**2B**	5	**3dB**	89
8	**1d**	**2C**	5	**3dC**	71
9	**1d**	**2D**	20	**3dD**	79
10	**1e**	**2A**	30	**3eA**	58
11	**1e**	**2B**	30	**3eB**	65
12	**1f**	**2A**	30	**3fA**	78

† The exclusive formation of a single regioisomer from the cycloaddition of **1** and the 2-substituted 1,3-diene **2B** or **2C** may be explained in terms of the difference in the stability of the intermediary carbenium ion (tertiary *vs.* secondary); the ion **1** (as an α-thiocarbocation) predominantly attacks one of the double bonds in the 1,3-diene in the direction of formation of a more stable tertiary carbenium ion intermediate, followed by attack of sulfur on the conjugated allyl cation resulting in ring closure.



Scheme 1



Scheme 2

Table 2 Reactions of cycloadduct **3dA** with base[a]

Entry	Base	Solvent	*T*/°C	Product yield (%)	
				4	**5** (diastereoisomeric ratio[b])
1	LDA	THF, N_2	−78 to 0	48	31(1 : 1.4)
2	NaH	DMF, N_2	0	42	31(1 : 1.2)
3	Et_3N	EtOH	0	51	28(1 : 1.2)
4	Et_2NH	$ClCH_2CH_2Cl$	R.t.	54	20(1 : 1.1)
5	AcOK	$ClCH_2CH_2Cl$	R.t.	45	27(1 : 1.1)
6	K_2CO_3	Acetone	R.t.	34	35(1 : 1.1)

[a] LDA = lithium diisopropylamide; THF = tetrahydrofuran; DMF = dimethylformamide. R.t. = room temperature. [b] Determined by ^1H NMR spectroscopy.

or 2-phenylbuta-1,3-diene **2c** afforded cycloadducts regiospecifically in all cases (entries 2, 4, 7, 8 and 11).† Buta-1,3-diene **2D** reacted only with the activated ion **1d** to give the corresponding cycloadduct in reasonable yield (entry 9).

We next studied the transformation of the cycloadducts to compounds having a new skeleton, the cycloadducts have sulfonium ion structures, and performed the reaction of the cycloadduct **3dA** with various bases with a view to its ring transformation. The results are summarized in Table 2. Strong and weak bases both caused a similar ring transformation to give the spiro compound **4** and the peroxide **5**, the latter compound as a diastereoisomeric mixture.

The formation of the peroxide is particularly interesting from a mechanistic point of view, so we investigated it in detail. When this reaction was performed with bubbling oxygen under the conditions of entry 3, the yield of the peroxide **5** increased to 73% and that of the spiro compound **4** decreased to 7%. However, even when the reaction was performed under N_2 (entries 1 and 2), the peroxide was obtained in similar yield as under an air atmosphere. This suggests that the peroxide might be formed by oxygen capture of the rather labile product during purification. Indeed, the ^1H NMR spectrum of a mixture of the cycloadduct **3dA** and potassium acetate in $CDCl_3$ in an NMR tube showed multiplet peaks corresponding to the terminal methylene protons at δ 4.81–5.01 and two pairs of doublets at δ 1.08 and 1.62 and at δ 1.22 and 1.48, which are assignable to the cyclopropane ring protons of the presumed labile diastereoisomeric intermediate **7**. After 6 h, the NMR measurement was performed again. Signals corresponding to cyclopropane ring protons were absent, but signals due to the spiro compound **4** appeared.

Based on the above results, we propose the following mechanism for formation of products **4** and **5**. The most acidic proton adjacent to sulfur in **3dA** is deprotonated with base to give the intermediate **6**, which is subsequently degraded *via* a 2,3-sigmatropic rearrangement into the cyclopropane intermediate **7**. The cyclopropane ring of the intermediate **7** may be cleaved to give the biradical intermediate **8**, probably because of stabilisation by captodative substituents, and by allyl resonance. This radical fission of a cyclopropane ring was reported in the *cis–trans*-isomerisation of captodatively substituted cyclopropanes.[2,3] The biradical intermediate **8** then recombines as the terminal methylene carbon to furnish product **4**, or is trapped with oxygen to give the peroxide **5**

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