Generation and reactions of butadienylthionium ions from 2-vinylcyclopropyl sulfoxides under Pummerer conditions

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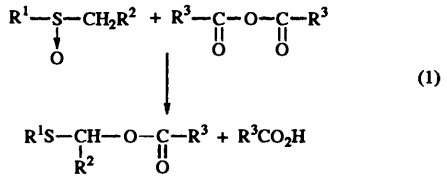
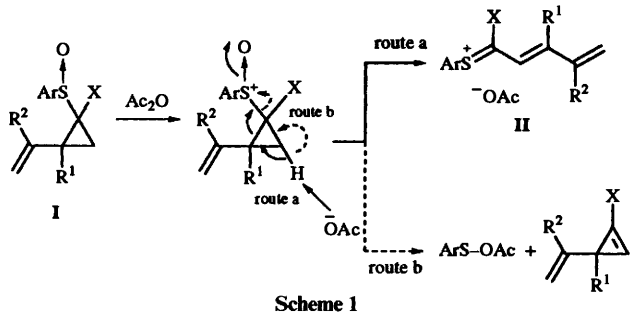
Treatment of 2-vinylcyclopropyl sulfoxides lacking an α-hydrogen with acid anhydrides produced butadienylthionium ion intermediates to give cyclic or acyclic conjugated dienes.

The Pummerer reaction of sulfoxides [eqn. (1)] is a useful method for the synthesis of α-substituted or α,β-unsaturated sulfides and has been significantly studied from both



(1)

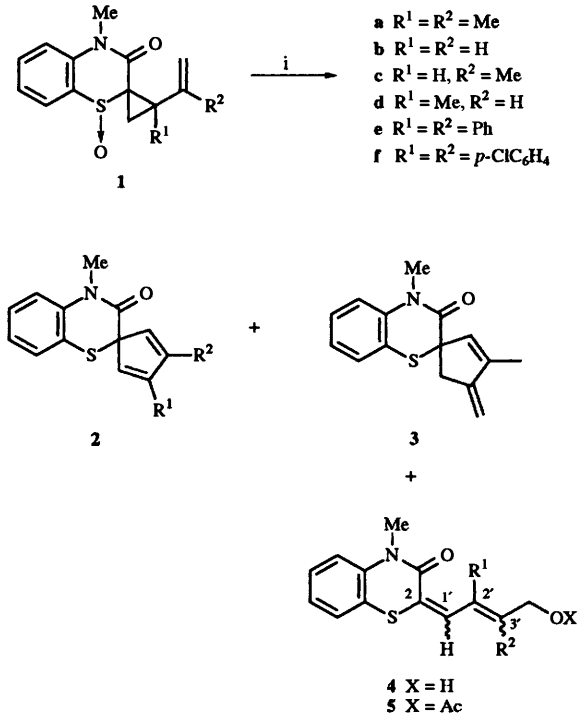
mechanistic and synthetic points of view.[1] The general mechanism of the reaction is believed to consist of four sequential steps involving a thionium ion intermediate.[2] Generation of vinylthionium ions has been widely investigated in the Pummerer reactions of allyl sulfoxides[3] and in the vinylogous Pummerer reactions of vinyl sulfoxides.[3c,e,4] In contrast, little attention has been paid to generation of butadienylthionium ions by the Pummerer reaction of sulfoxides.[5] The butadienylthionium ions are very versatile for the synthesis of functionalised conjugated dienes and we intend to explore a new method to generate them. It is known that sulfoxides lacking an α-hydrogen and carrying β-ones undergo the abnormal Pummerer reaction *via* sulfenic acid derivatives formed by β-hydrogen abstraction and C–S bond cleavage.[6] If 2-vinylcyclopropyl sulfoxides **I** without an α-hydrogen are treated with acid anhydrides, a butadienylthionium ion **II** would be generated by the destruction of a cyclopropane ring accompanied by β-hydrogen elimination (Scheme 1, route a)



Scheme 1

rather than a vinylcyclopropene by the abnormal Pummerer reaction (route b) because of the high energy content of the three-membered ring. For this strategy, we selected as substrates, 1,4-benzothiazin-3-one 1-oxides without an α-hydrogen, because they were easily prepared from 4-methyl-1,4-benzothiazin-3-one[7] in good yields by vinylcyclopropanation[8] followed by *m*-chloroperbenzoic acid (MCPBA) oxidation. In this communication, we report the novel generation of butadienylthionium ion intermediates by the reactions of 2-vinylcyclopropyl sulfoxides lacking an α-hydrogen with acid anhydrides.

Several 2-vinylcyclopropyl sulfoxides **1** were treated under Pummerer conditions: Method A, 2 equiv. of trifluoroacetic



Scheme 2 *Reagents and conditions:* i, Method A: 2 equiv. of TFAA, CH_2Cl_2, room temp., 2 h; Method B: 5 equiv. of Ac_2O, *p*-Me-$C_6H_4SO_3H$ (cat.), benzene, 85 °C, sealed tube, 24 h

anhydride (TFAA) in CH_2Cl_2 at room temperature for 2 h; Method B: 5 equiv. of Ac_2O and catalytic amount of *p*-$MeC_6H_4SO_3H$ in benzene at 85 °C in sealed tube for 24 h (Scheme 2). The results are summarised in Table 1. Reactions of disubstituted vinylcyclopropanes, **1a** ($R^1 = R^2 = Me$), **1e** ($R^1 = R^2 = Ph$) and **1f** ($R^1 = R^2 = p$-Cl–C_6H_4), with 2 equiv. of TFAA (Method A) furnished the cyclic dienes, **2a** and **3a**, **2e** and **2f**, in moderate yields, respectively (entries 1, 7 and 8). On the other hand, treatment of un- or mono-substituted vinylcyclopropanes, **1b** ($R^1 = R^2 = H$), **1c** ($R^1 = H$, $R^2 = Me$) and **1d** ($R^1 = Me$, $R^2 = H$), afforded acyclic conjugated dienes, **4b** or **5b**, **4c** and **4d**, respectively (entries 3–6). The dienol **4** was obtained by hydrolysis of corresponding dienyl trifluoroacetates initially formed during work-up. A mixture of **1c** and **1d** (*ca.* 2:1)†[8b] when allowed to react by Method A, provided **4c** in 70% yield. However, **4d**, which was observed in the ^1H NMR spectrum of crude products, could not be isolated becuase of its instability to silica gel (entry 5). The geometry at the C(2′)–C(3′) double bond ($\Delta^{2',3'}$) of the acyclic dienes **4** and **5**

† A mixture of 2-vinylcyclopropyl sulfoxides **1c** and **1d** (*ca.* 2:1) was prepared as follows: 4-methyl-1,4-benzothiazin-3-one was chlorinated with *N*-chlorosuccinimide, and the resultant α-chloro sulfide was treated with $AgClO_4$ in the presence of isoprene and then triethylamine followed by MCPBA oxidation.

Table 1 Reactions of 2-vinylcyclopropyl sulfoxides **1** with acid anhydrides

Entry	Sulfoxides	Conditions[a]	Products (% yields)[b]
1	**1a**	A	**2a** (25), **3a** (46)
2	**1a**	B	**2a** (21), **3a** (19)
3	**1b**	A	**4b** (*E*, 81)[d]
4	**1b**	B	**5b** (*E*, 39)[d]
5	**1c**:**1d** (*ca.* 2:1)[c]	A	**4c** (*E*, 70),[e] **4d** (—)[f]
6	**1d**	A	**4d** (*E*:*Z* = 1:1, 62)[g]
7	**1e**	A	**2e** (54)
8	**1f**	A	**2f** (60)

[a] Method A: 2 equiv. of TFAA, CH_2Cl_2, room temp., 2 h; Method B: 5 equiv. of Ac_2O, *p*-$MeC_6H_4SO_3H$ (cat.), benzene, 85 °C, sealed tube, 24 h. [b] Isolated yields unless otherwise mentioned. [c] The ratio was determined by ^1H NMR. [d] The geometry of $\Delta^{2',3'}$ was determined from the coupling constant in ^1H NMR. No geometrical isomer was isolated. [e] The geometry of $\Delta^{2',3'}$ was determined by NOE. No geometrical isomer was isolated. [f] Compound **4d** was observed in the ^1H NMR spectrum of crude products, but decomposed during purification by preparative TLC on silica gel. [g] Crude yield. The geometry of $\Delta^{2',3'}$ was determined by NOE and the ratio was estimated by ^1H NMR.

was determined from the coupling constant between 2'-H and 3'-H (**4b**: *J* 15, **5b**: *J* 15) in the ^1H NMR spectrum or by the NOE technique (**4c**, **4d**), and the geometry of $\Delta^{2,1'}$ of **4** and **5**, which consist of a single isomer, cannot at present be confirmed. In no case was any abnormal Pummerer-type product isolated.

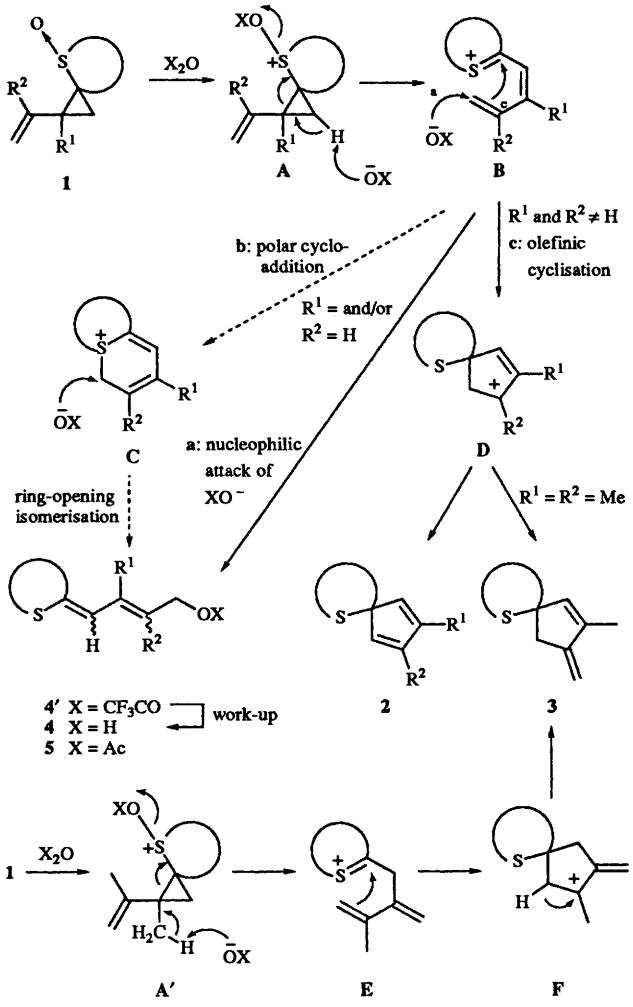
A possible mechanism for this Pummerer reaction is illustrated in Scheme 3. A butadienylthionium ion **B** generated by ring-opening of a cyclopropane ring with the elimination of a ring proton from an oxysulfonium salt **A**, which is initially formed by the reaction of a sulfoxide **1** with an acid anhydride. In the case of R^1 and/or R^2 = H, the intermediate **B** might follow either of two pathways to give an acyclic diene. One is nucleophilic attack process (a) of XO^- at the ε-carbon of **B** to provide a trifluoroacetate **4'**, which is hydrolysed to the corresponding dienol **4** during work-up, or an acetate **5**. The other is an intramolecular $[2^+ + 4]$ polar cycloaddition[8,9] process (b). The resultant bicyclic sulfonium salt **C** reacts with XO^- to give an acyclic diene, whose double bond may be isomerised under reaction conditions. In other cases (R^1 = R^2 = Me or Ar), a cyclic diene **2** is formed *via* a carbocation **D** generated by the olefinic cyclisation[10] of a thionium ion **B**. When both R^1 and R^2 are methyl groups, deprotonation of a methyl hydrogen from the carbocation **D** affords another cyclic diene **3**. The diene **3** may be given *via* processes of ring-opening of an oxysulfonium salt **A'** accompanied by methyl-proton abstraction, olefinic cyclisation of a thionium ion **E** and deprotonation of a carbocation **F**.

In summary, reactions of 2-vinylcyclopropyl sulfoxides lacking an α-hydrogen with acid anhydrides such as TFAA or Ac_2O provided cyclic or acyclic conjugated dienes *via* butadienylthionium ions. Extensive studies on this Pummerer reaction of various 2-vinylcyclopropyl sulfoxides are in progress.

Experimental

General procedure for the Pummerer reaction

Method A. To a solution of the 2-vinylcyclopropyl sulfoxide **1** (0.5 mmol) in dry CH_2Cl_2 (5 cm^3) was added TFAA (210 mg, 1.0 mmol) at room temperature. After 2 h, saturated aqueous $NaHCO_3$ was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 cm^3). The combined organic layer and extracts were dried ($MgSO_4$) and concentrated. The residue was purified



Scheme 3

by preparative TLC on silica gel eluting with hexane–ethyl acetate (4:1, v/v) to give the conjugated dienes **2** and **3** or **4** as shown in Table 1.

Method B. A mixture of compound **1** (0.5 mmol), Ac_2O (255 mg, 2.5 mmol) and *p*-TsOH·H_2O (10 mg, 0.05 mmol) in benzene (10 cm^3) was heated at 85 °C in sealed tube for 24 h. The reaction mixture was cooled and concentrated and the residue was purified by preparative TLC on silica gel eluting with hexane–ethyl acetate (4:1, v/v) to give **2** and **3** or **5** as shown in Table 1.

References

1 For reviews see: S. Oae and T. Numata, in *Isotopes in Organic Chemistry*, ed. E. Buncel and C. C. Lee, Elsevier, New York, 1980, **5**, 45; S. Oae, T. Numata and T. Yoshimura, in *The Chemistry of the Sulfonium Group*, ed. C. J. M. Stirling and S. Patai, Wiley, New York, 1981, **2**, 571; O. D. Lucchi, U. Miotti and G. Modena, *Org. React. (N. Y.)*, 1991, **40**, 157.

2 C. R. Johnson, J. C. Sharp and W. G. Phillips, *Tetrahedron Lett.*, 1967, 5299.

3 (*a*) G. A. Koppel and L. J. McShane, *J. Am. Chem. Soc.*, 1978, **100**, 288; (*b*) I. Cutting and P. J. Parsons, *Tetrahedron Lett.*, 1981, **22**, 2021; (*c*) R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, 1983, **24**, 2619; (*d*) R. D. Miller and R. Hässig, *Tetrahedron Lett.*, 1984, **25**, 5351; (*e*) R. Hunter and C. D. Simon, *Tetrahedron Lett.*, 1986, **27**, 1385; (*f*) Y. Kita, O. Tamura, F. Itoh, H. Yasuda, T. Miki and Y. Tamura, *Chem. Pharm. Bull.*, 1987, **35**, 562; (*g*) T. Iishihara, T. Shinozaki and M. Kuroboshi, *Chem. Lett.*, 1989, 1369; (*h*) R. Hunter, L. Carlton, P. F. Cirillo, J. P. Michael, C. D. Simon and D. S. Walter, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1631; (*i*)

R. Hunter, J. P. Michael, C. D. Siomn and D. S. Walter, *Tetrahedron*, 1994, **50**, 9365.
4 H. Kosugi, H. Uda and S. Yamagiwa, *J. Chem. Soc., Chem. Commun.*, 1975, 192; S. Yamagiwa, H. Sato, N. Hoshi, H. Kosugi and H. Uda, *J. Chem. Soc., Perkin Trans. 1*, 1979, 570.
5 E. J. Corey and D. J. Hoover, *Tetrahedron Lett.*, 1982, **23**, 3463.
6 R. B. Morin, D. O. Spry and R. A. Mueller, *Tetrahedron Lett.*, 1969, 849; R. B. Morin and D. O. Spry, *J. Chem. Soc., Chem. Commun.*, 1970, 335; F. Chioccara, L. Oliva and G. Prota, *Synthesis*, 1978, 744; M. Hori, T. Kataoka, H. Shimizu and Y. Imai, *Chem. Pharm. Bull.*, 1979, **27**, 1982; M. Hori, T. Kataoka, H. Shimizu and N. Ueda, *Tetrahedron Lett.*, 1981, **22**, 1701; H. Shimizu, N. Ueda, T. Kataoka and M. Hori, *Chem. Pharm. Bull.*, 1984, **32**, 2571.
7 H. Tawada, Y. Sugiyama, H. Ikeda, Y. Yamamoto and K. Meguro, *Chem. Pharm. Bull.*, 1990, **38**, 1238.
8 (*a*) H. Ishibashi, M. Okada, H. Nakatani and M. Ikeda, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1763; (*b*) T. Kataoka, unpublished work.
9 E. J. Corey and S. W. Walinsky, *J. Am. Chem. Soc.*, 1972, **94**, 8932; K. Fuji, S. P. Khanapure, M. Node, T. Kawabata, A. Itoh and Y. Masaki, *Tetrahedron*, 1990, **46**, 7393; H. Shimizu, S. Miyazaki, T. Kataoka and M. Hori, *Tetrahedron Lett.*, 1991, **32**, 5571; H. Shimizu, S. Miyazaki, T. Kataoka and M. Hori, *J. Chem. Soc., Chem. Commun.*, 1992, 1586.
10 Y. Tamura, H. Maeda, S. Akai and H. Ishibashi, *Tetrahedron Lett.*, 1982, **23**, 2209; H. Ishibashi, M. Okada, H. Komatsu, M. Ikeda and Y. Tamura, *Synthesis*, 1985, 643; H. Ishibashi, H. Ozeki and M. Ikeda, *J. Chem. Soc., Chem. Commun.*, 1986, 654; H. Ishibashi, S. Harada, M. Okada, M. Ikeda, K. Ishiyama, H. Yamashita and Y. Tamura, *Synthesis*, 1986, 847.

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