Tetrahedron Letters,Vol.30,No.21,pp 2797-2800,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

THERMOLYSIS OF THE SULFUR DIOXIDE ADDUCTS OF BENZOBENZVALENE. THE 1.3-DIPOLAR BEHAVIOUR OF A SULFENE

by Ulrich Burger*, Dominique Erne-Zellweger, Adam W. Sledeski and Serge Schmidlin.
Département de Chimie Organique, Université de Genève,
CH-1211 Genève 4, Switzerland.

Summary. Pyrolysis (fvp) of a strained γ-sultine (3) produced 1H-indene-1-carboxaldehyde (8) and naphthalene. The key step in the production of aldehyde (8) involves a 1,3-dipolar cycloreversion, as evidenced by the trapping of an intermediate sulfene (6) with methyl acrylate. A diradical pathway is proposed for the formation of naphthalene.

Sulfur dioxide reacts smoothly at low temperature with benzobenzvalene **1**[1] to give the crystalline sulfone 2 (m.p. 113-114.5 °C) and the γ-sultine **3** (m.p. 134-135 °C(decomp.)). These products were formed in ether at -50 °C in a 1:3 ratio and were isolated in 54 % total yield by medium pressure chromatography (silica gel, hexane/ethyl acetate, 2:3)[2,3]. The structure of these adducts was expected by analogy to the known reaction of other bridged bicyclo[1.1.0]butanes [4], including the parent benzvalene [5], with sulfur dioxide.

Concentrating on cycloreversion reactions of highly strained heterocyclic compounds [6] we decided to examine the thermolytic behaviour of the adducts 2 and 3, both, under the conditions of flash vacuum pyrolysis (fvp) and, in solution [7].

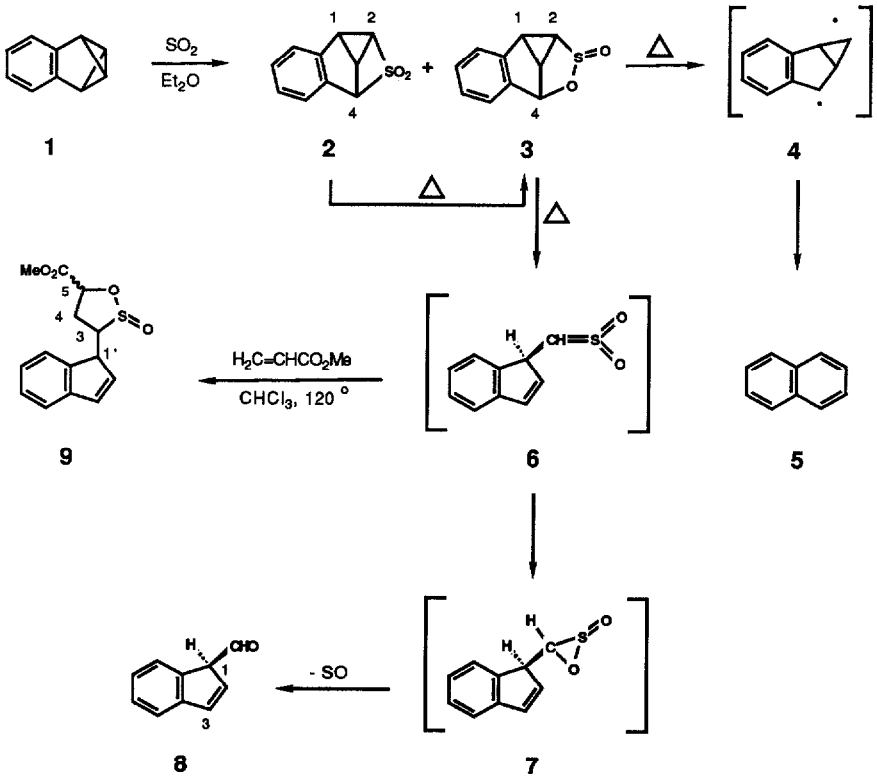
In a flow reactor operating at $5 \cdot 10^{-6}$ Torr and 650 K the sulfone 2 gave, in order of decreasing yield, naphthalene, the isomeric 1- and 3-indenecarboxaldehydes, γ-sultine 3, and a trace of indene. Relative yields are listed under entry A in the table. In this experiment the total yield of products with low molecular weight, was modest (30±5%) due to polymerization in the reactor. A much cleaner pyrolysis with a better overall yield (85±5%) was obtained with the γ-sultine 3 as the starting material. At 650 K it gave the same products as the sulfone 2, and in essentially the same proportions (table, entry B). In an experiment run at 750 K conversion of the γ-sultine 3 was complete, but a fairly large amount of indene (9.0 %) was formed at the expense of indenecarboxaldehyde (entry C of the table).

The gas phase thermolysis of various phenyl substituted γ-sultines has been reported to give cyclopropanes *via* a diradical pathway [8]. Therefore, in the light of these reports the formation of naphthalene from compound 3 is not unexpected. The sulfone 2 leads to the same result as it obviously rearranges first into 3. This latter process has ample precedent [4, 5]. Loss of sulfur dioxide in a homolytic process leading to the diradical 4, thus provides a ra-

tional for the formation of naphthalene. Of course, other pathways including heterolytic ones could equally well account for its occurence.

The mechanism leading to the indenecarboxaldehydes is less obvious. Certainly, the non-conjugate 1H-indene-1-carboxaldehyde **8** [9] is the kinetic product which subsequently gives the conjugate isomer. More importantly, the reaction mechanism must account for the fact that the oxygen atom of the aldehyde functionality is not originally bound to the correct carbon atom in the sultine **3**. We propose that compound **3** undergoes a thermal opening to give a sulfene, **6**, with subsequent ring closure (**6**→**7**) creating the required carbon-oxygen bond. The final step would then consist of loss of sulfur monoxide from the oxathiirane S-oxide **7** with concomittant release of the aldehyde **8** (scheme). Similar mechanisms have been previously considered for related reactions [10], and arguments in favour of the formation of the ephemeral sulfur monoxide have been presented [4].

Scheme



Formally, the process **3**→**6** amounts to a 1,3-dipolar cycloreversion, without necessarily being concerted [11]. This suggested to us that the resulting sulfene **6** may behave, in it's own right, as a 1,3-dipolar reagent. Considering it's electronic structure [12], we chose methyl

acrylate for the following trapping experiment, *i.e.* use was made of a dipolarophile with a notoriously low lying LUMO [13,14].

Thermolysis of the γ-sultine **3** at 398 K under argon in a sealed, acid free $CHCl_3$ or CH_2Cl_2 solution, gave, once again, 1H-indene-3-carboxaldehyde and naphthalene. ^{1}H-NMR spectroscopy showed a 1.3:1 ratio in favour of the aldehyde with *ca.* 30% conversion [15]. At higher conversion, or in less polar solvents including benzene, polymerization was preponderant. When we repeated the thermolysis of **3** in methylene chloride but with a tenfold excess of methyl acrylate present, we obtained the carbomethoxysultines **9** (mixture of stereoisomers) [16] in 58% isolated yield. The formation of indenecarboxaldehyde was suppressed in this experiment, but naphthalene was still produced, though in comparatively low yield (*ca.* 22%).

The carbomethoxysultines **9** clearly result from a regiospecific interception, *i.e.*, the former sulfene carbon atom is bound in all stereoisomers of **9** to the terminal carbon atom of the acrylate. These findings provide strong support for the mechanistic scheme outlined above. Moreover, they reveal unusual 1,3-dipolar reactivity of a sulfene. For the more common involvement of sulfenes in [4+2] and [2+2] cycloadditions see *e.g.* [17] and the references cited therein.

TABLE. Products and yield of fast vacuum pyrolyses at 5.10^{-6} Torr.

Entry	A	B	C
Starting material	**2**	**3**	**3**
Temperature [K]	650	650	750
Products and relative yield [%] (by NMR) :			
γ-sultine (**3**)	9.5	11	0
1H-indene-1-carboxaldehyde (**8**)	22	20.5	9.5
1H-indene-3-carboxaldehyde	16	13	12.5
indene	0.5	0.5	9.0
naphthalene	52	55	69
Total yield of isolated products [%]	30±5	85±5	85±5

The authors wish to express their gratitude to Mrs *E. Pamingle-Cristoforetti* (syntheses) and Mr. *J.-P. Saulnier* (NMR). Financial support was provided by the *Swiss National Science Foundation* (grant no. 20-5376.87).

REFERENCES AND NOTES

1 T.J. Katz, E.J. Wang, N.Acton, *J.Am.Chem.Soc.* **1971**, 93, 3782.

2 All new compounds gave satisfactory elemental analyses (C,H, and S) or high resolution mass spectra. The ^{1}H- and ^{13}C-NMR spectra are fully consistent with the structures indicated. m.p. of new compounds see text.

3 Selected spectroscopic data (for numbering see the scheme). Compound 2: ^{1}H-NMR (200 MHz, $CDCl_3$): 3.22(t,J=5.9,H-C(1)); 3.68(ddd,J=5.9, 5.7, 3.9,H-C(3)); 3.81(ddd,J=5.9, 5.7,3.2,H-C(2)); 5.13(dd,J=3.9, 3.2,H-C(4)); 7.2-7.5(m,4H). ^{13}C-NMR(50 MHz, $CDCl_3$): 8·CH at 32.4; 36.5; 53.9(C(2)); 83.0(C(4)); 123.9; 124.8; 128.0, and 129.7; 2·C at 137.6, and 138.7. Compound 3: ^{1}H-NMR(360 MHz, C_6D_6): 2.03(dd, J=6.0, 5.8, H-C(1)); 2.55(ddd, J=6.0, 5.8, 5.0, H-C(3)); 2.85(t, J=6.0, H-C(2)); 5.62(d, J=5.0, H-C(4)); 6.80-6.94(m, 4H). ^{13}C-NMR (50 MHz, $CDCl_3$): 34.5(C(1)); 36.3(C(3)); 66.6(C(2)); 91.8(C(4)); 4·CH at 124.1; 124.8; 127.8, and 129.9; 2·C at 138.0, and 142.0.

4 H. Hogeveen, L. Zwart, *J.Am.Chem.Soc.* **1982**, *104*, 4889.

5 M. Christl, E. Brunn, F. Lanzendörfer, *J.Am.Chem.Soc.* **1984**, *106*, 373.

6 a) U. Burger, Y. Mentha, P.J. Thorel, *Helv.Chim.Acta* **1986**, *69*, 670. b) U. Burger, P.J.Thorel, Y. Mentha, *Chimia* **1987**, *41*, 26.

7 For a review on flash vacuum thermolysis see *e.g.* a) R.F.C. Brown, 'Pyrolytic methods in organic chemistry', Academic Press 1980. b) U.E. Wiersum, *Recl.Trav. Chim.Pays-Bas* **1982**, *101*, 317; 365. c) U.E. Wiersum, *Aldrichimica Acta* **1984**,*17*, 31.

8 T. Durst, J.D. Finlay, D.J.H. Smith, *J.Chem.Soc.,Perkin Trans.* I. **1979**. 950.

9 Yu.I. Fedorov, E.B. Soboleva, G.A. Voskoboinik. *Zh.Vses.Khim.O-va.* **1976**, *21*, 346. (C.A. **85** 142234h).

10 a) J.F. King, P. de Mayo, C.L. McIntosh, K. Piers, D.J.H. Smith, *Can.J.Chem.* **1970**, *48*, 3704. b) A. Battaglia, A. Dondoni, G. Maccagnani, G. Mazzanti, *J.Chem.Soc., Perkin Trans.* II. **1974**, 609.

11 For review on 1,3-dipolar cycloreversions see *e.g.* G. Bianchi, R. Gandolfi in '1,3-Dipolar Cycloaddition Chemistry' A. Padwa, editor, Vol. 2, 451, John Wiley, New York, 1984.

12 J.P. Snyder, *J.Org.Chem.* **1973**, *38*, 3965.

13 J. Geittner, R. Huisgen, R. Sustmann, *Tetrahedron Lett.* **1977**, *18*, 881.

14 a) R.Sustmann, *Tetrahedron Lett.* **1971**, 2721. b) K.N. Houk, K. Yamaguchi in '1,3-Dipolar Cycloaddition Chemistry' A. Padwa, editor, Vol. 2, 407, John Wiley, New York, 1984.

15 Note that under these conditions γ-sultine **3** is the only source of oxygen available, and consequently, the oxygen atom of the ensuing aldehyde functionality must stem from compound **3**.

16 Five diastereoisomers (ratio *ca.*6:3:3:2:1) have been isolated by prep. tlc. All of them were obtained as colourless oils. The relative stereochemistry at the four chiral centers is at present unknown. The principal constituent has the following spectroscopic data (for numbering see the scheme): ^{1}H-NMR(360 MHz, $CDCl_3$): 2.49(ddd, J=13, 7, 2, 1H); 2.86(dt, J=13, 9, 1H); 3.13(ddd, J=13, 9, 7, H-C(3)); 3.76(s, OCH_3); 3.98(ddd, J=9, 2, 1.5, H-C(1'); 5.40(dd, J=9, 2, H-C(5));, 6.49(dd, J=6, 2, 1H); 6.93(dd, J=6, 1.5, 1H); 7.25-7.70(m, 4H). ^{13}C-NMR(50 MHz, $CDCl_3$): 31.37(CH_2); 47.57(CH); 52.85(CH_3); 8·CH at 68.82, 82.93, 121.7, 123.6, 125.6, 127.7, 133.6 and 135.7; 143.7(C); 144.5(C); 169.7(CO).

17 a) G. Opitz, *Angew.Chem.* **1967**, *79*, 161; *Angew.Chem.Int.Ed.* **1967**, *6*, 107. b) B.G. Lenz, B. Zwanenburg *in Houben-Weyl, Methoden der Org. Chemie* . Band E-11 Teil 2, 1326, Thieme Stuttgart, 1985. c) E. Block, M. Aslam, *Tetrahedron Lett.* **1982**, *23*, 4202 d) E.Block, A. Wall, *J.Org. Chem.* **1987**, *52*, 809. e)E.Smart, W.J. Middleton, *J.Am.Chem.Soc.* **1987**, *109*, 4982.

(Received in France 24 March 1989)