THE RAMBERG-BÄCKLUND PROCESS IN THE FRAGMENTATION OF TWO BENZYLIC β -DISULFONES

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Abstract—A new fragmentation process is reported for two benzylic β -disulfones. The proposed fragmentation scheme is analogous to the Ramberg-Bäcklund rearrangement of α -halosulfones in aqueous base.

INTRODUCTION

RECENTLY we have had occasion to prepare the benzylic β -disulfone (I). As expected, the mass spectrum of this compound is dominated by the tropylium ion and fragments derived therefrom. In addition to these ions, a pair of ions at m/e 104/105 were observed. We subsequently embarked upon a study of these ions, their compositions, likely structures and possible pathways of formation.

An examination of the literature showed that the mass spectrometry of sulfones has received a substantial amount of attention¹⁻⁸ since the paper by Meyerson, Drews and Fields¹ was published in 1964. Several processes have been invoked in order to rationalize the mass spectra of sulfones. Among the more important of these are α -H-migration,⁵ γ -H-migration⁵ and alkyl/aryl group migration from sulfur to oxygen,^{2,6-8} resulting in reorganization of the sulfone to a sulfinate ester.

RESULTS AND DISCUSSION

A high resolution mass spectrum of the β -disulfone (I) established the relevant ion masses as 104.0625 and 105.0703, requiring the compositions C₈H₈ and C₈H₉, respectively. This result necessitates incorporation of the phenyl ring in the structure of these ions.

Our first approach to identifying the origin of the remaining carbon and hydrogen atoms was to prepare the C-1 dideuterated compound (II). The mass spectrum of this compound showed scrambling of the deuterium atoms into the phenyl ring and an ion pattern in the m/e 105 to 108 region (see Table 1), indicating the almost complete retention of the benzylic deuterium atoms in these ions. This result is best rationalized by assuming that scrambling occurs immediately upon electron-impact.

The mass spectrum of the C-3 dideuterated material (III) showed no scrambling of the label and high retention of deuterium in the ions of the m/e 105 to 108 region (*vide* Table 1). Thus, the C-3 methylene group must be incorporated in the original m/e 104/105 ions of I.

Both C-1 and C-3 could be included in the m/e 104/105 ion structures. The formation of an ion at m/e 104 requires that a hydrogen atom be abstracted from either C-1 or C-3. Some ambiguity remained because of the scrambling of the benzylic hydrogen atoms. In order to examine this problem we prepared the C-3

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FIG. 1. Mass spectrum of PhCH₂·SO₂·CH₂·SO₂·CH₃ at 30 eV.

dichloro analog (IV). If analogous ions appeared in its spectrum (i.e. m/e 172, 173) this would suggest that the process under investigation gives rise to the m/e 104 ion by abstraction of a benzylic hydrogen rather than abstraction of a hydrogen atom from C-3. The mass spectrum of IV displays the expected ions at m/e 171.9845 (C₈H₆Cl₂) and m/e 172.9925 (C₈H₇Cl₂).

In view of the established tendency for γ -H-migration,⁵ the potential for double migration in these systems is very striking. C-1 and C-5 are mutually γ , as are C-1 and both oxygen atoms of the S-4 sulfonyl group. Furthermore, C-5 is γ to both oxygen atoms of the S-2 sulfonyl group. Due to the scrambling of the benzylic hydrogens, it was not possible to decide from the mass spectra of II and III, whether there is any exchange between the methyl group and the benzylic methylene, since even in compound II protium atoms are primarily abstracted from the benzylic site. It was, therefore, mandatory that a sample of material preferentially labeled at C-5-be prepared, since scrambling would not affect the observation of deuterium atoms transferred to the benzylic position.

Compound <i>m/e</i>	104	105	106	107	108
(I)	6.7	9.5	1	_	
(II)	—	4·1	6.8	9.5	1.4
(III)	—	3.5	8.8	10.5	3.5
(V)	8.9	19.0	14.3	4·7	

Table 1. Percentage relative abundance^a of ions in the m/e 104 to 108 region of deuterated β -disulfones and the parent β -disulfone (I)

^a Relative abundances are reported as percentages of the base peak of each spectrum (m/e 91). Due to varying deuterium incorporation in the tropylium ion, the relative abundance of the other ions changes. However, the ratio of the total intensity of the ions at m/e 91 to 94 to the total intensity of the ions at m/e 104 to 108 is essentially constant at 1:0.18 for all compounds (I, II, III and V).



FIG. 2. Mass spectrum of PhCH₂·SO₂·CCl₂·SO₂·CH₃ at 30 eV.

A sample of heptadeuterated I was prepared and back-exchanged furnishing compound V. Unfortunately, the back-exchange left C-1 only partly re-exchanged. Examination of the m/e 104 to 107 region of the mass spectrum of V (see Table 1) led to the conclusion that the ions were 7.9:7.6:3.3, nondeuterated:monodeuterated: dideuterated, respectively. Assuming that the observed labeling was exclusively a result of incomplete back-exchange at C-1, a simple calculation indicates that the benzylic position was overall 37% deuterated. The n.m.r. showed that the benzylic hydrogens had a relative intensity of 1.26 H or 63% of normal intensity. It follows that C-5 is not included in the m/e 104/105 ions and that double exchange does not occur to any significant extent. The mass spectrum of V also clearly indicated that the m/e 105 ion of compound I retained the original hydrogen atoms of C-1 and C-3.

At this point the possibility remained that the m/e 105 ion in the mass spectrum of I could essentially be giving rise to all the ions at m/e 104. A single fragmentation scheme would then account for both ions. The mass spectrum of I was recorded at a number of ionization potentials to see if the ratio of the intensities of these ions remained constant. Variation of the ratio would suggest that they originated from different processes, while a constant ratio would suggest that they might arise one from the other. The results of this study are presented in Table 2.

These results indicate that at least half of the m/e 104 ions come from some source other than the m/e 105 ions.

1 2 3 4 5 $PhCX_2:SO_2:CY_2:SO_2:CZ_3$ (I) X, Y, Z = H (II) Y, Z = H; X = D (III) X, Z = H; Y = D (IV) X, Z = H; Y = CI (V) X, Y = H; Z = D

m/e 104/105 Intensity ratio ^a		

Table 2. Dependence of the m/e 104/105 ion intensity ratios on ionizing voltage

* Ratio remained constant over the 30 to 70 eV range.

A priori, there is little reason to suppose that either sulfonyl group in I is the more readily ionized. Ionization of the S-4 sulfonyl group followed by γ -H-migration rationalizes the ultimate appearance of the m/e 104 ion rather satisfactorily. Ionization of the S-2 sulfonyl group followed by α -H-migration provides a rationale for the ultimate appearance of the m/e 105 ion. Both processes are depicted in Scheme 1.



SCHEME 1

This new fragmentation scheme, which we are proposing to rationalize the formation of the m/e 104 ion in particular, is very similar to the well known Ramberg-Bäcklund rearrangement^{9,10} of α -halosulfones. In solution it is essential that the substrate be a sulfone in order that the sulfur atom be lost as SO₂ from the intermediate episulfone. α -Halosulfoxides and α -halosulfides do not undergo the Ramberg-Bäcklund rearrangement. We have prepared both the sulfone–sulfide (VI) and the

E
PhCH₂:S·CH₂:SO₂·CH₃
(VI)
$$E = \text{Lone pair}$$

(VII) $E = 0$

sulfone-sulfoxide (VII), and have found no m/e 104/105 ions in the mass spectrum of either compound. Thus, the analogy between this new fragmentation process and the Ramberg-Bäcklund rearrangement is complete.

CONCLUSIONS

The mass spectra of two benzylic β -disulfones contain ions which can be rationalized in terms of a Ramberg-Bäcklund process. A complete study of the process including the examination of selectively deuterated samples, accurate mass determinations for the key ions, an investigation of structural dependence and an examination of the dependence of the intensity ratio of the key ions on ionizing voltage, is in good accord with the interpretation presented.

EXPERIMENTAL

General

The low resolution mass spectra were recorded on a Dupont-CEC Model 21-104 mass spectrometer. The samples were directly introduced using an all glass probe and the spectra run at 30 eV with a source temperature of 150 $^{\circ}$ C.

The high resolution mass spectra were recorded on a Dupont-CEC Model 21-110B double focusing mass spectrometer. The samples were directly introduced and the spectra run at 70 eV with a source temperature of 165 $^{\circ}$ C.

The n.m.r. spectra were obtained on samples in $CDCl_3$ solution with tetramethylsilane as the internal reference using a Varian T-60 instrument. The i.r. spectra were recorded on samples in $CHCl_3$ solution using a Perkin-Elmer 237-B grating spectrophotometer. All compounds were homogeneous on t.l.c.

Preparation of monochlorodimethyl sulfone.* A solution of monochlorodimethyl sulfide (50 g) in glacial acetic acid (100 ml) was added dropwise to a mixture of CrO_3 (125 g) in glacial acetic acid (100 ml) which had been preheated to 50 °C. The drop rate was adjusted so that the temperature of the reaction mixture was maintained between 90 to 100 °C by the exothermic reaction. Upon completion of the addition, ice-water (300 ml) was added and the aqueous solution extracted with $CHCl_3$ (ten 100 ml aliquots). The combined $CHCl_3$ layers were washed with 5% NaOH (100 ml aliquots) until the aqueous layer had a basic pH. The last aqueous wash was back-extracted with $CHCl_3$ (100 ml) after acidification. The $CHCl_3$ layers were dried (MgSO₄) and the $CHCl_3$ evaporated furnishing monochlorodimethyl sulfone (23 g). After recrystallization from 95% ethanol, the product had m.p. 57 to 58 °C; i.r. 1355, 1155 cm⁻¹ (ν_{So_2}); n.m.r. τ 6.97 (3H, s), 5.60 (2H, s).

Preparation of PhCH₂·S·CH₂·SO₂·CH₃ (VI)

Benzyl thiol (9.0 ml) was added to a solution of sodium metal (1.725 g) dissolved in absolute ethanol (100 ml). Monochlorodimethyl sulfone (7.999 g) was added and the solution refluxed for

* This procedure is a modification of the method of Truce et al.¹¹

1 h. Ice-water (150 ml) was added and the mixture extracted with CHCl_a (four 100 ml aliquots). The CHCl_a layers were dried (MgSO₄) and rotary evaporated furnishing the sulfone-sulfide (VI) (12.6 g). After recrystallization from 95% ethanol, the product had m.p. 64.5 to 65.5 °C; i.r. 1320, 1135 cm⁻¹ (ν SO₂); n.m.r. τ 7.00 (3H, s), 6.32 (2H, s), 5.96 (2H, s), 2.66 (5H, s). Found: C, 50.1; H, 5.6%, C₉H₁₂O₂S₂ requires C, 50.0; H, 5.6%.

Preparation of PhCH₂·S·CCl₂·SO₂·CH₃

A solution of sulfone-sulfide (VI) (27.0 g) in CH₂Cl₂ (180 ml) was brought to gentle reflux and a solution of sulfuryl chloride (35.0 g) in CH₂Cl₂ (180 ml) was added dropwise over 2.5 h. Upon completion of addition the solution was refluxed for another 0.5 h. The methylene chloride was rotary evaporated and the residue recrystallized from 95% ethanol furnishing the *dichlorosulfone-sulfide* (31.8 g). The product had m.p. 53 to 55 °C; i.r. 1330, 1150 cm⁻¹ (ν SO₂); n.m.r. τ 6.67 (3H, s), 5.63 (2H, s), 2.73 (5H, s). Found: C, 37.9; H, 3.4%. C₈H₁₀Cl₂O₂S₂ requires C, 37.9; H, 3.5%.

Preparation of the β -disulfones I and IV

These β -disulfones were prepared from the corresponding sulfone-sulfides by the procedure of Truce *et al.*¹¹

PhCH₂·SO₂·CH₂·SO₂·CH₃ (I) was obtained in 67% yield. After recrystallization from 95% ethanol it had m.p. 157 to 158.5 °C; i.r. 1330, 1325, 1130, 1125 cm⁻¹ (ν SO₂); n.m.r. τ 6.77 (3H, s), 5.83 (2H, s), 5.40 (2H, s), 2.63 (5H, s). Found: C, 43.5; H, 4.9%. C₃H₁₂O₄S₂ requires C, 43.5; H, 4.9%.

PhCH₂·SO₂·CCl₂·SO₂·CH₃ (IV) was obtained in 92% yield. After recrystallization from 95% ethanol it had m.p. 101.5 to 103 °C; i.r. 1355, 1340, 1150 cm⁻¹ (ν SO₂); n.m.r. τ 6.53 (3H, s), 5.10 (2H, s), 2.63 (5H, s). Found: C, 34.0; H, 3.1%. C₉H₁₀Cl₂O₄S₂ requires C, 34.1; H, 3.2%.

Preparation of PhCH₂·SO·CH₂·SO₂·CH₃ (VII)

A solution of the sulfone-sulfide (VI) (1.999 g) in methanol (50 ml) was added to a cooled solution of sodium metaperiodate (1.997 g) in water (25 ml) over a period of 3 min. The resulting mixture was stirred at 0 °C for 17 h. The ice bath was removed and the mixture stirred for an additional 7 h. Water (100 ml) was added to the reaction mixture and the resultant solution washed with CHCl₃ (three 100 ml aliquots). The combined CHCl₃ layers were dried (MgSO₄), filtered and the CHCl₃ rotary evaporated furnishing crude sulfone-sulfoxide. The crude material was chromatographed on silica gel (120 g) with CHCl₃ (100 ml fractions). The sulfone-sulfoxide (1.008 g) was isolated from fractions 7 to 11 inclusive. The chromatographed product was recrystallized from 95% ethanol furnishing platelets, m.p. 139 to 141 °C; i.r. 1325, 1150 cm⁻¹ (ν SO₂), 1055 cm⁻¹ (ν SO); n.m.r. τ 6.87 (3H, s), 6.03 (2H, q, J = 4 Hz), 5.70 (2H, q, J = 12 Hz), 2.63 (5H, s). Found: C, 46·1%; H, 5·2%, C₉H₁₂O₃S₂ requires C, 46·5; H, 5·2%.

Preparation of PhCD₂·SO₂·CD₂·SO₂·CH₃

The β -disulfone (I) (105 mg) was refluxed in CH₃CH₂OD (5 ml) and D₂O (5 drops) for 23 h. The solution was cooled to room temperature and stored at 0 °C for 1 h. The crystals (90 mg) were filtered and dried ($\frac{9}{0} d_2 3 \cdot 8$, $d_3 26$, $d_4 58 \cdot 5$, $d_5 11 \cdot 7$).

Preparation of PhCD₂·SO₂·CH₂·SO₂·CH₃ (II)

PhCD₂·SO₂·CD₂·SO₂·CH₃ (48.8 mg) was refluxed in 95% ethanol (3 ml) for 1 h. The solution was cooled to room temperature and stored at 0 °C for 1 h. The crystals (36.4 mg) were filtered and dried (% d_1 14.1, d_2 63.6, d_3 17.7, d_4 4.6).

Preparation of PhCH₂·SO₂·CD₂·SO₂·CH₃·(III)

The β -disulfone (I) was refluxed in CH₃CH₂OD (5 ml) and D₂O (5 drops) for 5 min. The reaction flask was immediately immersed in an ice/water bath and the resultant crystals (91 mg) filtered and dried (% d_0 4·2, d_1 20·7, d_2 64·9, d_3 9·9).

Preparation of PhCD₂·SO₂·CD₂·SO₂·CD₃

The β -disulfone (I) (222.5 mg) was refluxed in a solution of sodium metal (21 mg) dissolved in CH₃OD (10 ml) for 3 h. CH₃OD (5 ml) was distilled off and the residue cooled to 0 °C for 2 h. The

crystals (184 mg) were filtered, washed with D_2O and recrystallized from CH_3CH_2OD/D_2O furnishing the heptadeuterated compound (103 mg) which was identical with undeuterated I by i.r., t.l.c., m.p. and mixed m.p. (% d_4 2.9, d_5 13.0, d_6 36.7, d_7 47.2)

Preparation of PhCH₂·SO₂·CH₂·SO₂·CD₃ (V)

Recrystallized heptadeuterated I (39.3 mg) was refluxed in 95% ethanol (3 ml) and 0.0025 N NaOH (3 drops) for 1 h. The solvent was rotary evaporated and the residue recrystallized from 95% ethanol (1.5 ml) and H₂O (0.5 ml). The crystals (15.4 mg) were filtered and dried (% d_1 3.0, d_2 16.9, d_3 45.4, d_4 28.6, d_5 6.0).

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