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FURTHER INVESTIGATION OF THE RAMBERG-BÄCKLUND PROCESS

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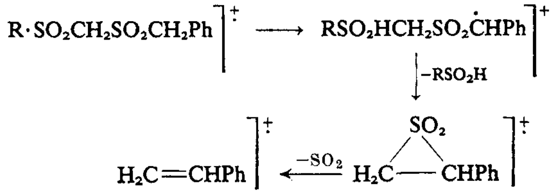
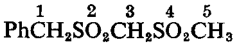
Abstract—A further examination of the Ramberg-Bäcklund process in the mass spectra of β-disulfones is reported. An alternative rationale is dismissed from consideration and additional evidence adduced for preferential abstraction of benzylic hydrogens by γ-sulfonyl groups.

INTRODUCTION

THE MASS spectra of sulfones have received a substantial amount of attention over the last decade.[1–3] In a previous article[1] we have reported the mass spectrum of the benzylic β-disulfone (I) and suggested pathways for the formation of ions at *m/e* 104 (C_8H_8) and 105 (C_8H_9). The proposed Ramberg-Bäcklund process for the formation of the *m/e* 104 ion would proceed via H abstraction from C-1 by an oxygen atom on S-4, loss of methanesulfinic acid with concomitant episulfone formation, followed by loss of SO_2 to give rise to the molecular ion of styrene (see Scheme 1). A parallel process is proposed for *m/e* 105.



SCHEME 1. The Ramberg-Bäcklund process.



$$\overset{1}{\mathrm{PhCH_2}}\overset{2}{\mathrm{SO_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{SO_2}}\overset{5}{\mathrm{CH_3}}$$

(I)

To exclude both exchange of hydrogen atoms between C-5 and C-1, as well as involvement of C-5 in the *m/e* 104, 105 ion structures, we prepared and examined the mass spectrum of I, preferentially deuterated at C-5. Unfortunately, the material was still partially deuterated at C-1 which complicated the analysis of the results.

RESULTS AND DISCUSSION

We have subsequently prepared two more benzylic β-disulfones (II and III). The spectra of these compounds show the presence of the expected ions at *m/e* 104, 105. The spectrum of the phenyl β-disulfone (II) is particularly interesting. The fact that the Ramberg-Bäcklund process occurs for this system indicates that the *m/e* 104, 105 ions do not require a methyl group on S-4 and therefore C-5 of compound (I) is not contained in the *m/e* 104, 105 ions in the spectrum of I, as indicated by the labeling study reported previously.[1]

$PhCH_2SO_2CH_2SO_2R$
(II) $R = Ph$
(III) $R = ClCH_2$

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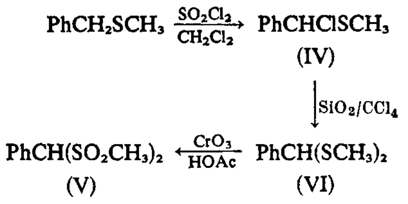
A reasonable alternative rationale for the appearance of ions at *m/e* 104, 105 was proposed by a referee of the previous paper.[1] The alternative process would proceed by loss of the methylsulfonyl group from the molecular ion of I, hydrogen atom migration from C-1 to C-3 (giving rise to ion *b* in Scheme 3), methyl migration to C-1 followed by loss of SO_2 to furnish the *m/e* 105 ion. The *m/e* 104 ion might then form in part from the *m/e* 105 ion or by an entirely independent process. In the initial paper[1] we presented evidence which was designed to show that the *m/e* 104 ion was best rationalized as forming by a Ramberg-Bäcklund process. Little attention was directed to the ion at *m/e* 105.

In order to examine the possibility that the *m/e* 105 ion was arising by this alternative process and if so, to see whether or not an ion also appeared at *m/e* 104, we decided to prepare a compound which would produce the $Ph\dot{C}HSO_2CH_3]^+$ ion. Such a compound would have to be a benzyl methyl sulfone which contained a labile group attached to the benzylic carbon. We have found[1,4] that the methylsulfonyl group is itself a very labile group and consequently chose the preparation of bismethylsulfonyl phenylmethane (V) as our objective.

The β-disulfone (V) was a known compound[5,6] which had been previously prepared from α-chlorobenzyl methyl sulfide (IV) by hydrolysis to furnish the β-disulfide (VI) followed by peroxide oxidation to give the β-disulfone (V). The hydrolysis of IV gives rise to VI contaminated with benzaldehyde.[6]

We have abbreviated the synthesis of V in a useful fashion by employing a reaction which we first observed on α-chlorodibenzyl sulfide.† When α-chlorodibenzyl sulfide was subjected to column chromatography employing carbon tetrachloride and silica gel, pure bisthiobenzyl phenylmethane was obtained directly. Application of this reaction to α-chlorobenzyl methyl sulfide (IV) furnished the β-disulfide (VI) which did not require further purification. Oxidation of VI with Fieser's reagent furnished V. The synthesis is depicted in Scheme 2.



$$PhCH_2SCH_3 \xrightarrow[CH_2Cl_2]{SO_2Cl_2} \underset{(IV)}{PhCHClSCH_3} \xrightarrow{SiO_2/CCl_4} \underset{(VI)}{PhCH(SCH_3)_2} \xrightarrow[HOAc]{CrO_3} \underset{(V)}{PhCH(SO_2CH_3)_2}$$

SCHEME 2

The β-disulfone (V) did indeed furnish a mass spectrum with the desired ion at *m/e* 169·0323 ($C_8H_9O_2S$). This ion did not give rise to an ion at *m/e* 104, thereby completely removing it from consideration as a precursor for the production of the *m/e* 104 ions in the mass spectrum of the β-disulfone (I).

The appearance of an ion at *m/e* 107·0494 (C_7H_7O) in the mass spectrum of V is excellent support for the failure of the *m/e* 169 ion to intervene in the mass spectrum of I since it has no ion at *m/e* 107.

The most interesting feature of the mass spectrum of V was the appearance of an ion at *m/e* 105, in accord with the expectation generated by the alternative fragmentation pattern outlined previously. However, accurate mass determination for this ion

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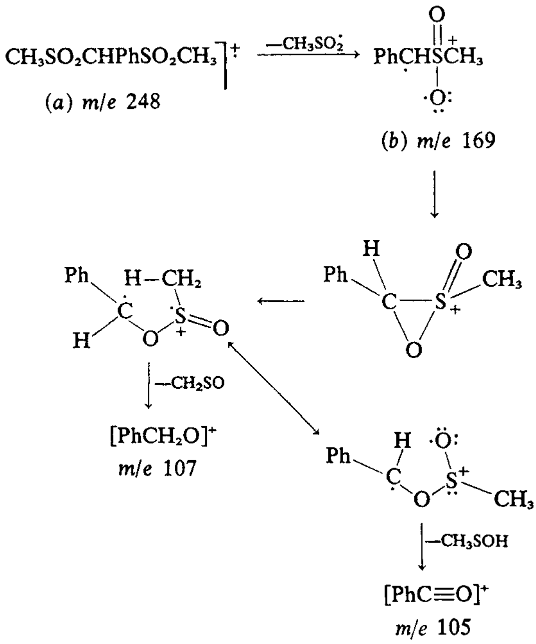
† J. S. Grossert, W. R. Hardstaff and R. F. Langler, unpublished results.

established its composition to be C_7H_5O (*m/e* 105·0339) and not C_8H_9 as required by the alternative hypothesis.

It is now evident that the *m/e* 169 ion does not intervene in the formation of either the *m/e* 104 or *m/e* 105 ions from the molecular ion of I. Therefore, the Ramberg-Bäcklund process[1] provides the best rationale for the appearance of both the *m/e* 104 (C_8H_8) and *m/e* 105 (C_8H_9) ions in the mass spectra of I, II and III.

It is also significant that a Ramberg-Bäcklund process might be expected to occur during the fragmentation of the molecular ion of V. The fact that it does not occur highlights the importance of labile benzylic hydrogen atoms being present in a γ-relationship to a sulfonyl group, as is the case for compounds I, II and III.

The mass spectrum of V can be satisfactorily rationalized by invoking accepted processes which we have summarized previously.[1] A proposed fragmentation scheme is outlined in Scheme 3.



Scheme 3

CONCLUSIONS

The preparation of $(CH_3SO_2)_2CHPh$ (V), which is isomeric with the previously examined[1] $CH_3SO_2CH_2SO_2CH_2Ph$ (I), has permitted an examination of the fragmentation of the $CH_3SO_2\dot{C}HPh]^+$ ion and demonstrated that it does not form pursuant to electron-impact on I. The previously proposed Ramberg-Bäcklund process is the best rationale for the appearance of both the *m/e* 104 (C_8H_8) and 105 (C_8H_9) ions in the mass spectrum of I.

EXPERIMENTAL

General

The low resolution mass spectra were recorded on a Dupont 21-490 instrument. The samples were directly introduced and the spectra run at 30 eV with a source temperature of 200 °C.

The high resolution mass spectra were recorded on an AEI 902 mass spectrometer at 70 eV with a source temperature of 200 °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 Beckman I.R.-10 grating spectrophotometer. All compounds were homogeneous on t.l.c.

Preparation of $PhCH_2SO_2CH_2SO_2Ph$ (II). $PhCH_2SCH_2SO_2Ph$ (0·0988 g)[7] was added to a mixture of chromium trioxide (0·1132 g) in glacial acetic acid (15 ml). The solution was heated to 90 to 100 °C for 0·5 h. Water (50 ml) was added and the solution extracted with chloroform (four 50 ml aliquots). The combined chloroform layers were washed with 2·5 % NaOH (50 ml aliquots) until the pH of the aqueous layer remained basic. The final aqueous wash was neutralized with concentrated HCl and back-extracted with chloroform (50 ml). The combined chloroform layers were dried ($MgSO_4$)s filtered and rotary evaporated furnishing crude β-disulfone (106·6 mg). The crude product wa. recrystallized from 95 % ethanol affording clean β-disulfone which had m.p. 151 to 151·5 °C; i.r; 1340, 1148, 1130 cm^{-1}. (ν_{SO_2}); n.m.r. τ 5·70 (2H, s), 5·36 (2H, s), 2·36 (10H, m). Found: C, 54·0, H, 4·6%. $C_{14}H_{14}O_4S_2$ requires C, 54·2; H, 4·5%.

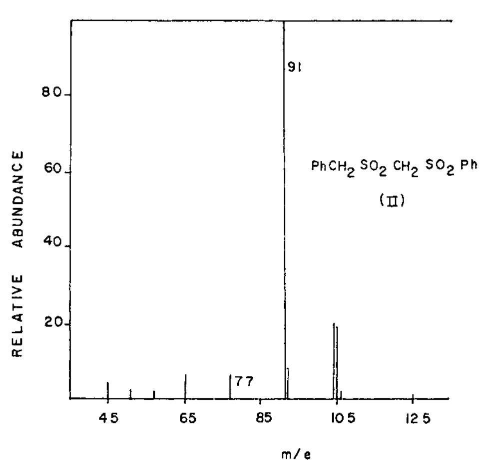


Fig. 1. Mass spectrum of $PhCH_2SO_2CH_2SO_2Ph$ (II) at 30 eV.

Preparation of $PhCH_2SCH_2SO_2CH_2Cl$. Bischloromethyl sulfone (5·061 g)[8] was added to a solution of sodium metal (0·785 g) and benzyl thiol (4·2 ml) in absolute ethanol (100 ml). The solution was refluxed for 1 h 10 min and water (100 ml) was added. The mixture was extracted with chloroform (three 100 ml aliquots). The combined chloroform layers were dried ($MgSO_4$), filtered and the chloroform rotary evaporated. The residue was chromatographed on silica gel (360 g) using chloroform (100 ml aliquots) as eluant. The product was isolated from fractions 9 to 22 inclusive, but was still contaminated with unreacted bischloromethyl sulfone. The chromatographed sulfone–sulfide was dissolved in chloroform (75 ml) and washed with 2·5 % NaOH (nine 50 ml aliquots). The chloroform was dried ($MgSO_4$), filtered and rotary evaporated. The residue was recrystallized from 95 % ethanol (3X), yielding pure sulfone–sulfide (1·140 g). The product had m.p. 79 to 81 °C; i.r. 1330, 1150 cm^{-1} (ν_{SO_2}); n.m.r. τ 6·23 (2H, s), 6·00 (2H, s), 5·36 (2H, s), 2·80 (5H, s). Found: C, 43·2; H, 4·4%. $C_9H_{11}ClO_2S_2$ requires C, 43·1; H, 4·4%.

Preparation of $PhCH_2SO_2CH_2SO_2CH_2Cl$ (III). $PhCH_2SCH_2SO_2CH_2Cl$ (0·206 g) was added to glacial acetic acid (50 ml) and chromium trioxide (0·199 g). The reaction mixture was heated to 90 to 100 °C for 0·5 h. Water (50 ml) was added and the solution extracted with chloroform (four 50 ml aliquots). The combined chloroform layers were washed with 2·5 % NaOH (50 ml aliquots) until the pH of the aqueous layer remained basic. The last wash was acidified and back-extracted with chloroform (100 ml). The combined chloroform layers were dried ($MgSO_4$), filtered and rotary evaporated affording crude β-disulfone (170·7 mg). The residue was recrystallized from 95 % ethanol,

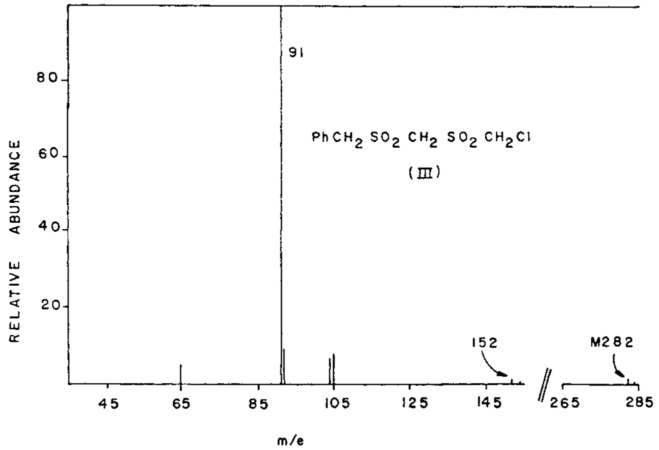


FIG. 2. Mass spectrum of $PhCH_2SO_2CH_2SO_2CH_2Cl$ (III) at 30 eV.

furnishing the β-disulfone which had m.p. 156 to 158 °C; i.r. 1340, 1135, 1120 cm^{-1} (ν_{SO_2}); n.m.r. τ 5·66 (2H, s), 5·43 (2H, s), 5·16 (2H, s), 2·63 (5H, s). Found: C, 38·4; H, 3·8%. $C_9H_{11}ClO_4S_2$ requires C, 38·2; H, 3·9%.

Preparation of $PhCH(SCH_3)_2$ (VI). α-Chlorobenzyl methyl sulfide (IV) was prepared as described by Bordwell *et al.*[9] α-Chlorobenzyl methyl sulfide (10·029 g) was chromatographed on a column of silica gel (250 g) employing carbon tetrachloride eluant (100 ml aliquots). Fractions 10 to 30 inclusive were combined to furnish bisthiomethyl phenylmethane (4·321 g). The product had m.p. 25 °C and n.m.r. τ 7·93 (6H, s), 5·20 (1H, s), 2·60 (5H, m).

Preparation of $PhCH(SO_2CH_3)_2$ (V). Bisthiomethyl phenylmethane (1·0038 g) was dissolved in glacial acetic acid (10 ml) and added to a mixture of chromium trioxide (2·443 g) in glacial acetic acid (100 ml). The reaction mixture was heated to 90 to 100 °C for 0·5 h. Water (100 ml) was added and the solution extracted with chloroform (four 100 ml aliquots). The combined chloroform layers were washed with 5% NaOH (100 ml aliquots) until the aqueous layer remained basic. The final base wash was acidified with concentrated HCl and back-extracted with chloroform (100 ml). The combined chloroform layers were dried ($MgSO_4$), filtered and the chloroform rotary evaporated. The residue was recrystallized from 95% ethanol affording bismethylsulfonyl phenylmethane (0·562 g) which had m.p. 161 to 163 °C; i.r. 1340, 1320, 1150, 1125 cm^{-1} (ν_{SO_2}); n.m.r. τ 6·76 (6H, s), 4·76 (1H, s), 2·46 (5H, m).

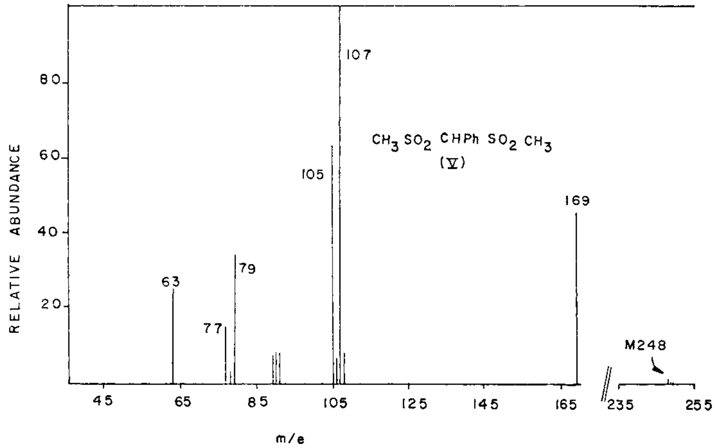


FIG. 3. Mass spectrum of $CH_3SO_2CHPhSO_2CH_3$ (V) at 30 eV.

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REFERENCES

1. W. R. Hardstaff and R. F. Langler, *Org. Mass Spectrom.* **10**, 215 (1975) and references therein.
2. A. A. Kutz and S. J. Weininger, *J. Org. Chem.* **33**, 4070 (1968).
3. I. Pratanata, L. R. Williams and R. N. Williams, *Org. Mass Spectrom.* **9**, 418 (1974).
4. W. R. Hardstaff, R. F. Langler and M. J. Newman, *Org. Mass Spectrom.* **9**, 1156 (1974).
5. H. J. Backer, *Rec. Trav. Chim.* **68**, 827 (1949).
6. H. J. Böhme and H. J. Gran, *Ann.* **577**, 68 (1952).
7. W. G. Phillips and K. W. Ratts, *J. Org. Chem.* **36**, 3145 (1971).
8. W. E. Truce, G. H. Birum and E. T. McBee, *J. Amer. Chem. Soc.* **74**, 3594 (1952).
9. F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.* **77**, 572 (1955).