

correlate this effect with the corresponding band width (BW). In the first-nearest-neighbor's approximation, the π -energy band of the zigzag planar sulfur chain in the framework of the EHT is

$$E(\mathbf{k}) = \frac{H + 2KSH \cos(\mathbf{k}\mathbf{a})}{1 + 2S \cos(\mathbf{k}\mathbf{a})} \quad (7)$$

where \mathbf{k} is the wave vector, S is the overlap integral, H is the valence-state ionization potential of the p_z orbital, \mathbf{a} is the lattice spacing, and K is the Wolfsberg-Helmholtz constant. The π -energy loss due to closed-shell repulsion in an energy band per repeat unit can be approximated by averaging over two \mathbf{k} points ($\mathbf{k} = 0.0$ and π/\mathbf{a}), and is given up to second order in overlap by

$$\Delta E \approx -16HS^2 \quad (8)$$

where $K = 2.0$. The corresponding BW is approximately given by

$$BW \approx |4HS| \quad (9)$$

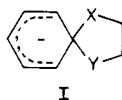
Because S^2 is greater than 0 and H is less than 0, the smaller the S , the smaller the repulsion. Thus, the narrower the band, the weaker the electron repulsions, and the relationship is approximately quadratic ($\Delta E \approx -(BW)^2/H$). In the case of polymeric sulfur, the polymer is forming a screw conformation to make the $3p_z$ orbitals almost orthogonal ($S \approx 0.0$). As an illustration, Figure 15 shows the averaged energy of the $(H^-)_x$ chain per H atom relative to the situation of no closed-shell repulsions as a function of the BW on the basis of the extended Hückel solid-state calculation (six \mathbf{k} points). The energy loss due to closed-shell repulsion is approximately quadratic in the BW up to 10-15 eV.

The Gas-Phase Smiles Rearrangement: A Heavy Atom Labeling Study

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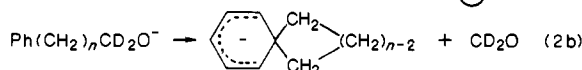
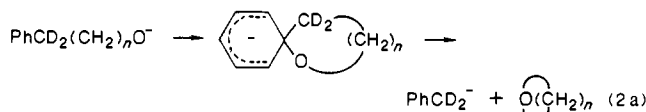
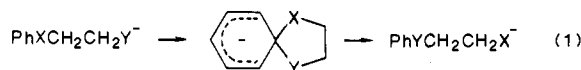
Contribution from the Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia, 5001, Australia, and Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0362. Received September 19, 1988

Abstract: Heavy atom (¹³C and ¹⁸O) labeling shows that the product ion PhO⁻ from PhO(CH₂)₂O⁻ and products PhO⁻ and PhS⁻ from PhS(CH₂)₂O⁻ are formed through Smiles intermediates I (X = Y = O or X = O, Y = S). The analogous product



ions from PhO(CH₂)₃O⁻ and PhS(CH₂)₃O⁻ are formed by two processes. It is likely that these are (i) Smiles and (ii) S_Ni attack by O⁻ at the methylene group PhXCH₂. The extent of the Smiles process decreases as n increases for systems PhX(CH₂) _{n} O⁻. The Smiles rearrangement does not occur for ions PhO(CH₂) _{n} S⁻ ($n = 2-6$).

The classical (condensed phase) Smiles rearrangement² is summarized in eq 1. The nucleophilic attack normally requires an electron-withdrawing group (e.g., nitro, sulfonyl, or halogen) either in the ortho or para position on the aromatic ring; generally X is a good leaving group, and Y is a strong nucleophile.³



Collisional activation of ions PhCD₂(CH₂) _{n} O⁻ ($n = 2-4$) in the gas phase result in the formation of PhCD₂⁻.⁴ The possibility of a Smiles rearrangement (eq 2a) was suggested although S_Ni attack at the β carbon (β to phenyl) could not be excluded. Similarly, ions Ph(CH₂) _{n} CD₂O⁻ ($n = 2$ and 3) eliminate CD₂O,

and a Smiles product ion (eq 2b) was proposed.⁵ We were not able to substantiate the mechanistic proposals shown in eq 2a and 2b, but if they are correct it means that gas-phase Smiles rearrangements do not require the activation of the benzene ring by an ortho or para electron-withdrawing group.

In this paper we report a study of gas-phase systems where the operation of Smiles rearrangements can be tested experimentally. We report the operation of gas-phase Smiles rearrangements for species related to those shown in eq 1, in particular when X = Y = O and when X = S and Y = O. The mechanisms are substantiated by heavy atom (¹³C, ¹⁸O) labeling studies.

Experimental Section

Collisional activation mass spectra (MS/MS) were recorded with a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical ionization mode.⁶ All slits were fully open to obtain maximum sensitivity and to minimize energy resolution effects.⁷ The chemical ionization slit was used in the ion source, ionizing energy 70 eV (tungsten filament); ion source temperature 150 °C; accelerating voltage -8 kV. Deprotonation of the appropriate neutral substrate was effected by HO⁻ (or H⁻ or O⁻). Reactant negative ions were generated from water with 70 eV electrons.⁸ The indicated source pressure of H₂O was

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(3) For a review, see: Truce, W. E.; Kreider, E. M.; Brand, W. W. *Organic Reactions*; John Wiley and Sons: New York, 1970; Vol. 18, pp 99. See, also: Schmidt, D. M.; Bonvicino, G. E. *J. Org. Chem.* **1984**, *49*, 1664 and references cited therein.

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Table I. CA Mass Spectra of PhX(CH₂)_nY⁻ Anions

parent ion	loss				abundance	formation					
	H ⁺	H ₂	CH ₂ O	PhOH		PhO ⁻		PhS ⁻			
						width ^a	collision induced ^b	abundance	width ^a	collision induced ^b	
PhO(CH ₂) ₂ O ⁻	15				100	40.5	30				
PhO(CH ₂) ₃ O ⁻	12				100	c	20				
PhO(CH ₂) ₄ O ⁻	16				100	39.5	60				
PhS(CH ₂) ₂ O ⁻	8	2	6		100	23.1	10	57	d	40	
PhS(CH ₂) ₃ O ⁻	8				100	47.7	20	36			
PhS(CH ₂) ₄ O ⁻	10				4			100		50	
PhS(CH ₂) ₅ O ⁻	8							100	47.5	45	
PhS(CH ₂) ₆ O ⁻	12							100	44.9	40	
PhOCH ₂ S ⁻	100			88	16						
PhO(CH ₂) ₂ S ⁻	100	15		52	26						
PhO(CH ₂) ₃ S ⁻	100	8		25	15						
PhO(CH ₂) ₄ S ⁻	72	5			100						
PhO(CH ₂) ₅ S ⁻	66	15			100						

^a Width of peak at half height (V) - error ± 0.5 V. ^b When a potential of +1000 V is applied to the collision cell, the original peak splits into two—the shifted peak is due to collision-induced dissociation occurring within the cell and the unshifted peak is due to dissociation outside (principally before) the collision cell. The listed figure refers to the percentage of shifted (collision induced) peak. ^c Composite peak—see Figure 2. ^d Composite peak—see Figure 3.

5×10^{-4} Torr. The substrate pressure (substrate introduced through the septum inlet at 150 °C) was typically 5×10^{-7} Torr. The estimated total pressure in the ion source is estimated to be 10^{-1} Torr. The pressure of He in the second collision cell was 2×10^{-7} Torr measured by an ion gauge situated between the electric sector and second collision cell. This produced a decrease in the main beam signal of ca. 10% and thus corresponds to essentially single collision conditions.

Consecutive collision induced dissociation spectra (MS/MS/MS) were measured with a Kratos MS 50-TA instrument described previously.⁹ In a typical experiment, a specific fragment ion M_2 formed in the MS/MS spectrum of M_1 was transmitted to the third field free region by setting both ESA-1 and the magnetic sector to (M_2/M_1) of the normal setting used to focus M_1 . Mass analysis of fragment ions resulting from collision induced decomposition in the third field free region was accomplished by scanning ESA-2. Neutral substrates were deprotonated by MeO⁻ (from MeONO¹⁰) in a Kratos Mark IV chemical ionization source: ion source temperature 100 °C, electron energy 280 eV, emission current 500 μ A, and accelerating voltage -8 kV. Liquids were introduced through an all-glass heated inlet system at 100 °C. The indicated source pressure of each substrate was 2×10^{-5} Torr and of methyl nitrite 1×10^{-6} Torr giving an estimated source pressure of 10^{-1} Torr. The indicated pressure of He in the collision cells was 2×10^{-6} Torr, producing a decrease in the main beam signals of 30%.

2-Phenoxyethanol was a commercial product. The following compounds were prepared by reported procedures: 3-phenoxypropanol,¹¹ 4-phenoxybutanol,¹¹ thiophenoxymethanol,¹² 2-thiophenoxyethanol,¹³ 3-thiophenoxypropanol,¹⁴ 4-thiophenoxybutanol,¹⁵ 5-thiophenoxy-pentanol,¹⁶ phenoxyethanethiol,¹⁷ 2-phenoxyethanethiol,¹⁸ 3-phenoxypropanethiol,¹⁹ 4-phenoxybutanethiol,²⁰ and 5-phenoxy-pentanethiol.²¹

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The Labeled Compounds. 2-Phenoxyethan-¹⁸O-ol and Related Compounds. A suspension of phenoxyacetic acid (1.52 g) in thionyl chloride (4.5 mL) was stirred at 35 °C for 5 h, the excess thionyl chloride was removed in vacuo, to the residue was added anhydrous tetrahydrofuran (1.5 mL) and H₂¹⁸O (Yeda Research and Development Co., 20.8% ¹⁸O, 300 mg), and the mixture was stirred at 20 °C for 2 h. Removal of the solvent gave a residue which was dried in vacuo (0.02 mm, 80 °C, 3 h), dissolved in anhydrous tetrahydrofuran (4 mL), and added dropwise at 0 °C over a 30-min period and under nitrogen to a stirring suspension of lithium aluminum hydride (474 mg) in anhydrous tetrahydrofuran (2 mL). The mixture was heated under reflux for 3 h and cooled to 10 °C, aqueous sodium sulfate (saturated, 1 mL) was added, and the mixture was dried (MgSO₄) and distilled to yield 2-phenoxyethan-¹⁸O-ol (1.01 g, 73% yield, ¹⁸O = 10%), bp 117.5–119 °C/20 mmHg.

3-Phenoxypropan-¹⁸O-ol and 4-phenoxybutan-¹⁸O-ol were prepared similarly in 87 and 84% yields, respectively.

2-(Phenoxy-¹³C)ethanol. (a) 1,5-(Dicyano-¹³C₂)pentane. A mixture of 1,5-dibromopentane (5.22 g), 18-crown-6 (0.40 g), and potassium cyanide-¹³C (Cambridge Isotopes, 99%, ¹³C, 3.0 g) in anhydrous acetonitrile (30 mL) was stirred at reflux for 16 h. On cooling to 20 °C, the mixture was filtered through silica gel (1-cm thickness in a 50-mL sintered glass funnel), the silica gel was washed with acetonitrile (2 \times 20 mL), and the filtrates were combined. Distillation gave 1,5-(dicyano-¹³C₂) pentane as a colorless oil (2.81 g, 99% yield), bp 119–120 °C/1.0 mmHg.

(b) Pentane-1,5(dicarboxylic acid-¹³C₂). 1,5-(Dicyano-¹³C₂)pentane (2.81 g), tetrahydrofuran (1 mL), and aqueous hydrogen chloride (concentrated, 8.5 mL) were heated under reflux for 6 h. The solution was cooled to 20 °C, the hydrolysis product was extracted into diethyl ether (5 \times 8 mL), washed with aqueous sodium chloride (saturated, 8 mL), and dried (MgSO₄). Removal of the solvent gave pentane-1,5(dicarboxylic acid-¹³C₂) (3.44 g, 94% yield), mp 103–105 °C (lit.²² 102–104 °C).

(c) Cyclohexanone-¹³C. Modification of Reported Procedure.²² A mixture of pentane-1,5(dicarboxylic acid-¹³C₂) (3.44 g) and barium carbonate-¹³C (British Oxygen Co., ¹³C = 62.8%, 225 mg) was heated at 305–310 °C (Woods metal bath) in an apparatus²² which allowed the product to distill out under a slow stream of nitrogen (5 mL min⁻¹). The cyclohexanone-¹³C (1.73 g, 82% yield) was used directly in the next step.

(d) Phenol-¹³C. Cyclohexanone-¹³C (1.73 g) was converted into phenol-¹³C (1.46 g, 88% yield) by a reported pyrolysis reaction²² using a mixed base metal catalyst.²³ ¹³C Incorporation (determined by positive ion mass spectrometry) = 99%. ¹³C NMR (Bruker WP 80 MHz instrument, solvent CDCl₃), 155.4 (C-1, singlet), other peaks, 129.9, 121.2, 113.7, less than 3% of C-1 peak height.

(e) 2-(Phenoxy-¹³C)ethanol. Phenol-¹³C (0.475 g) and ethylene oxide (2.40 mL) were heated at 40–45 °C for 48 h in a Carius tube. On cooling to 0 °C, the reaction vessel was opened, and the excess ethylene oxide was allowed to evaporate. Distillation at 10 mmHg, using a T tube

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(23) Mitsubishi Petrochemical Col. Ltd., Br. Patent 970835; *Chem. Abstr.* **1964**, *61*, 13240e.

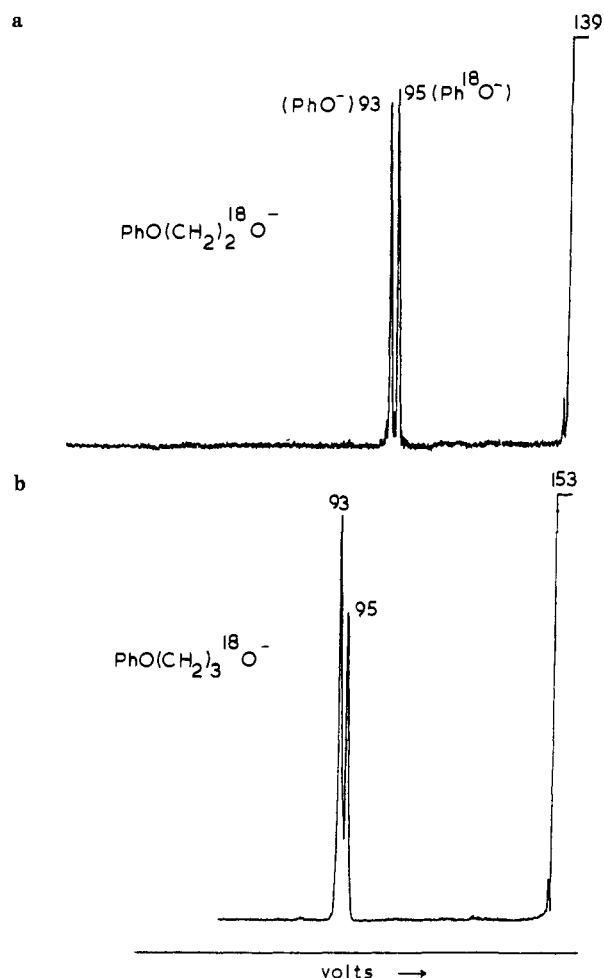


Figure 1. (A) Collisional activation mass spectrum of $\text{PhO}(\text{CH}_2)_2^{18}\text{O}^-$. (B) Collisional activation mass spectrum of $\text{PhO}(\text{CH}_2)_3^{18}\text{O}^-$. Experimental details—see Experimental Section.

in a sublimation block (110–120 °C) gave 2-(phenoxy- I - ^{13}C)ethanol (0.64 g, 91% yield). ^{13}C = 98%.

2-(Thiophenoxy- I - ^{13}C)ethanol. This was prepared by a seven stage synthesis from $\text{Me}^{13}\text{CO}_2\text{Na}$ (Cambridge Isotope Laboratories, ^{13}C = 99%). (a) The ^{13}C labeled sodium acetate was converted²⁴ into labeled ethyl acetate in 93% yield. The reaction²⁵ of ^{13}C labeled ethyl acetate with the bis Grignard reagent from 1,5-dibromopentane gave 1-(methyl- ^{13}C)-cyclohexan-1-ol in 87% yield.

(b) **1-(Methyl- ^{13}C)-cyclohex-1-ene.** 1-(Methyl- ^{13}C)-cyclohexan-1-ol (3.01 g) was heated at 135 °C in a distillation flask fitted with a vacuum jacketed Vigreux Column. Addition of one crystal of iodine at 10-min intervals on eight occasions gave a distillate which was a mixture of water and product. Separation of the organic phase followed by distillation gave 1-(methyl- ^{13}C)-cyclohex-1-ene (1.91 g, 75% yield), bp 104–106 °C/760 mmHg.

(c) Pyrolysis²² of 1-(methyl- ^{13}C)-cyclohex-1-ene using a mixed base metal catalyst²³ gave methyl(benzene- I - ^{13}C) in 91% yield. Oxidation²⁶ of the labeled toluene with potassium permanganate gave benzoic acid- I - ^{13}C in 90% yield, followed by Schmidt rearrangement²⁷ gave aniline- I - ^{13}C hydrochloride (91% yield), which was then converted²⁸ into thiophenol- I - ^{13}C in 71% yield. Thiophenol- I - ^{13}C was transformed into (thiophenoxy- I - ^{13}C) ethanol in 98% yield by a reported procedure.²⁹ ^{13}C = 99% (by positive ion mass spectrometry). ^{13}C NMR (Bruker WP 80 MHz instrument, solvent CDCl_3) 134.9 (C-1, s), other peaks 129.5, 128.7, 126.1, 60.1 and 36.2 less than 10% of C-1 peak height.

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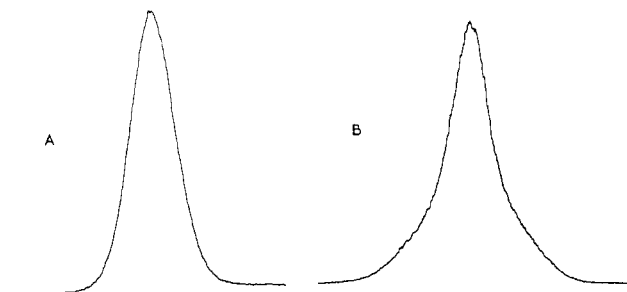


Figure 2. (A) PhO^- peak (m/z 93) from $\text{PhO}(\text{CH}_2)_2\text{O}^-$. Width of peak at half height = 40.5 ± 0.5 V. (B) PhO^- composite peak (m/z 93) from $\text{PhO}(\text{CH}_2)_3\text{O}^-$. Major component width at half height ca. 35 V; minor component ca. 105 V.

Results and Discussion

The collisional activation mass spectra of all species $\text{PhX}(\text{CH}_2)_n\text{Y}^-$ [$\text{X} = \text{O}$ or S , $\text{Y} = \text{O}$ or S , $n = 2$ –6] are listed in Table I. The base peak in the spectra of all species $\text{PhO}(\text{CH}_2)_n\text{O}^-$ ($n = 2$ –4) corresponds to PhO^- (m/z 93).³⁰ The question at issue is whether this product ion is formed through the intermediacy of a Smiles intermediate (see, e.g., eq 1) or by some other process. If a Smiles intermediate is uniquely involved, then both of the oxygen atoms of $\text{PhO}(\text{CH}_2)_n\text{O}^-$ must be involved equally in the formation of the product PhO^- . The collisional activation mass spectra of $\text{PhO}(\text{CH}_2)_n^{18}\text{O}^-$ ($n = 2$ and 3) are shown in Figure 1. When $n = 2$, the abundances of Ph^{16}O^- and Ph^{18}O^- are very nearly equal,³¹ whereas for $n = 3$ the abundance ratio $\text{Ph}^{16}\text{O}^-:\text{Ph}^{18}\text{O}^-$ is 100:76. In marked contrast, the spectrum of $\text{Ph}^{16}\text{O}(\text{CH}_2)_4^{18}\text{O}^-$ shows only Ph^{16}O^- .³² As a hypothesis we propose that (i) the phenoxide ions shown in Figure 1A are formed exclusively by a Smiles rearrangement (eq 3),³³ (ii) two processes form the ions shown in Figure 2b, viz. a Smiles rearrangement (eq 4), the major process, together with an $\text{S}_{\text{N}}1$ reaction (eq 5), and (iii) in the case of $\text{PhO}(\text{CH}_2)_4\text{O}^-$, the $\text{S}_{\text{N}}1$ process (cf. eq 5) occurs exclusively.³³

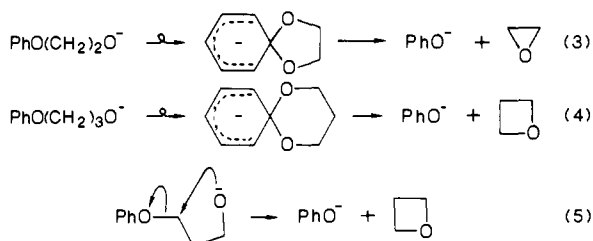
The occurrence of (i) two mechanisms for the formation of PhO^- from $\text{PhO}(\text{CH}_2)_3\text{O}^-$ (ii) a single mechanism for each of the analogous products from $\text{PhO}(\text{CH}_2)_n\text{O}^-$ ($n = 2$ and 4) is further

(30) The process(es) forming PhO^- must be facile since collisional activation is not required for the formation of product ions. In the data presented in Table I the collision-induced components of m/z 93 for $\text{PhO}(\text{CH}_2)_2\text{O}^-$ ($n = 2, 3,$ and 4) are 30, 20, and 60%, respectively.

(31) The abundance ratios of m/z 93:95 in Figure 1a are $(95 \pm 0.5):100$ (a mean of ten scans) corresponding to an isotope effect $^{16}\text{O}/^{18}\text{O}$ of 1.05 ± 0.003 in favor of the loss of $\text{C}_2\text{H}_4^{16}\text{O}$.

(32) The collisional activation mass spectrum of $\text{Ph}^{16}\text{O}(\text{CH}_2)_4^{18}\text{O}^-$ is as follows [$m/z(\text{loss})$ %]: 176 (H^+) 15 and 93 ($\text{C}_4\text{H}_8^{18}\text{O}$) 100.

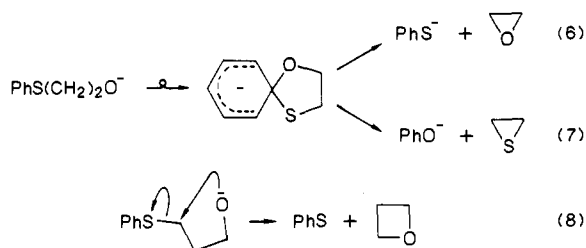
(33) (a) A referee has asked whether the negative ion technique is a suitable method for structure determination if this sort of rearrangement can occur so readily. Skeletal rearrangements in the spectra of even electron negative ions are in fact not common. We have reported a number of simple "rules" for the fragmentation of even electron negative ions (Raftery, M. J.; Bowie, J. H.; Sheldon, J. C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 563; *Int. J. Mass Spectrom. Ion Proc.* **1988**, 85, 167). Most fragmentations involve loss of a neutral molecule and are rationalized as proceeding via the charged center through ion complexes. When such reactions are unfavorable, either (i) proton transfer to the original center may produce a new anion which may fragment or (ii) if this is not possible, skeletal rearrangement may occur. (b) The most plausible decomposition pathway involves C–O bond cleavage of the Smiles intermediate followed by an $\text{S}_{\text{N}}1$ reaction to liberate ethylene oxide as the neutral species. A more complex reaction might involve C–O bond cleavage and hydride transfer to form ultimately acetaldehyde as the neutral product. We attempted neutralization/ionization experiments (Danis, P. O.; Wesdemiotis, C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1983**, 105, 7454. Burgers, P. C.; Holmes, J. L.; Mommsers, A. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1983**, 102, 1) in both the ZAB and MSS0 instruments in order to identify the neutral component. For example, the accelerating potential on the ZAB was set at -7 kV and a potential of -7.2 kV applied to the second collision cell thus deflecting the negative ion beam but allowing neutrals to pass through the collision cell. Ionization by He produced from the neutral(s) a positive ion spectrum which was monitored in the usual manner. Unfortunately, the spectrum produced was that of ionized benzene, thus masking the recognition of the $\text{C}_2\text{H}_4\text{O}$ species. The collision-induced loss of benzene does not yield a detectable negative ion in the spectrum suggesting that product negative ion is unstable with respect to its radical. The structure of the product is not known. The same result was obtained for the $\text{PhO}(\text{CH}_2)_4\text{O}^-$. The neutral products of eq 3–8 are designated as cyclic ethers or thioethers throughout this paper—their identities have not been confirmed.



substantiated by data shown in Figure 2 and Table I. Figure 2A shows the profile of the peak at m/z 93 formed from $\text{PhO}(\text{CH}_2)_2\text{O}^-$ —it has a single component of Gaussian shape. Figure 2B shows a composite peak: the major component a narrow peak (the Smiles process) superimposed on a broad peak (the S_{Ni} process). The corresponding peak from $\text{PhO}(\text{CH}_2)_4\text{O}^-$ is Gaussian in shape with only one component (see Table I).

In order to substantiate reaction through the Smiles intermediate shown in eq 3, it is necessary to prove that nucleophilic attack occurs specifically at the carbon which bears the initial substituent (C1) rather than, say, at an ortho position (C2). Thus the Smiles rearrangement of $\text{PhO}(\text{CH}_2)_2\text{O}^-$ labeled with ^{13}C at position 1 of the benzene ring should yield PhO^- labeled exclusively with ^{13}C at position 1. If such an experiment is to be meaningful, some method of determining the position of the label in the product ion must be available. Such a method is available, and the data are summarized in Figure 3. The characteristic collision-induced dissociations of PhO^- are losses of CO and CHO^* (Figure 3A); of (phenyl-2,4,6- D_3) O^- , CO , and CDO^* (Figure 3B);³⁴ and of (phenyl-1- ^{13}C) O^- , specifically ^{13}CO and $^{13}\text{CHO}^*$ (Figure 3C).³⁴ The MS/MS/MS spectrum of the product ion (m/z 94, $^{12}\text{C}_5^{13}\text{CH}_5\text{O}^-$) from (phenyl-1- ^{13}C) $\text{O}(\text{CH}_2)_2\text{O}^-$ shows exclusive loss of ^{13}CO (Figure 3D), thus substantiating the formation of the Smiles intermediate shown in eq 3.

The processes forming product ions from $\text{PhS}(\text{CH}_2)_2\text{O}^-$ ($n = 2-6$) are very similar to those described above for $\text{PhO}(\text{CH}_2)_2\text{O}^-$. The extent of the probable Smiles rearrangement can be seen by reference to Table I. When $n = 2$ or 3, PhO^- is the base peak of the spectrum with PhS^- being of smaller abundance; for $n = 5$ or 6, only PhS^- is observed. The data in Figure 4 show that PhS^- is formed by one process when $n = 2$ and by two processes when $n = 3$ (cf. Figure 2). Thus it is probable that the Smiles process occurs exclusively when $n = 2$ (eq 6 and 7); both the Smiles [cf. eq 6 (narrow component, Figure 4) and eq 7] and S_{Ni} process occur when $n = 3$, and the S_{Ni} process dominates when $n \geq 4$ (cf. eq 8).



In order to confirm that the reactions shown in eq 6 and 7 do proceed through a Smiles intermediate, we have carried out MS/MS/MS experiments (of the type outlined above) with the appropriate ^{13}C labeled derivatives. If the ion (phenyl-1- ^{13}C) $\text{S}(\text{CH}_2)_2\text{O}^-$ undergoes the Smiles rearrangement exclusively, the product ions PhO^- and PhS^- should each be specifically labeled at the 1 position with ^{13}C . The characteristic collision induced decompositions of these two ions should be exclusive loss of ^{13}CO and C_4H_4 ,³⁵ respectively. The MS/MS/MS spectra of the product ions show the expected losses,³⁶ substantiating the formation of

(34) These data show that PhO^- fragments without H or C scrambling of the phenyl ring. Such site specificity is also observed for PhS^- .³⁵ In contrast, other phenyl systems may undergo atom scrambling prior or during fragmentation (Raftery, M. J.; Bowie, J. H.; Sheldon, J. C. J. *Chem. Soc., Perkin Trans. 2* 1988, 255 and references cited therein).

(35) Bowie, J. H.; Stringer, M. B. *Org. Mass. Spectrom.* 1985, 20, 138.

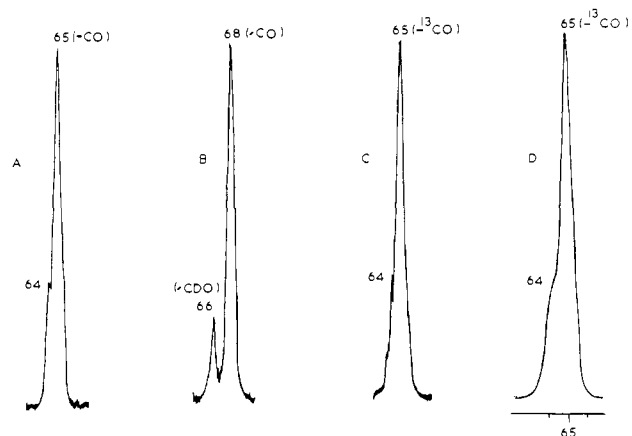


Figure 3. Partial collision-induced mass spectra (the m/z 64–66 region) of (A) PhO^- , (B) phenyl-2,4,6- D_3) O^- , (C) (phenyl-1- ^{13}C) O^- , and (D) of the m/z 94 ion from the 2-(phenoxy)-1- ^{13}C ethoxide ion.

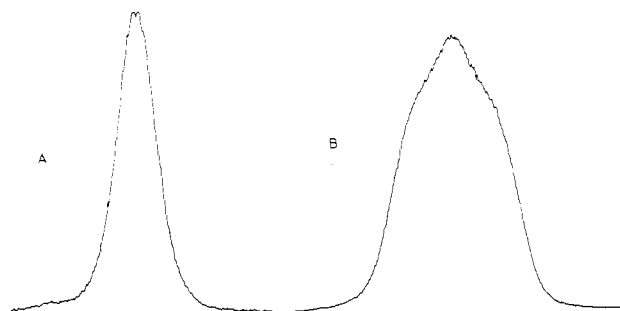


Figure 4. (A) PhS^- peak (m/z 109) from $\text{PhS}(\text{CH}_2)_2\text{O}^-$. Width of peak at half height = 46.0 ± 0.5 V. (B) PhS^- composite peak (m/z 109) from $\text{PhS}(\text{CH}_2)_3\text{O}^-$. Broad peak (S_{Ni} process—eq 8)—width at half height 96.0 ± 0.5 V.

the Smiles intermediate in the reactions shown in eq 6 and 7.

Finally, ions $\text{PhO}(\text{CH}_2)_n\text{S}^-$ ($n = 2-5$) do not undergo the Smiles rearrangement since no peaks corresponding to PhS^- are observed. Presumably S^- is not a strong enough nucleophile to effect this reaction, thus competitive pathways are preferred. For example, when $n = 2$ or 3 the characteristic fragmentation is loss of PhOH , whereas the S_{Ni} reaction leading to PhO^- is pronounced when $n = 4$ or 5 (cf. eq 5 and 8).

In conclusion, experimental evidence has been presented which establishes that Smiles intermediates are involved exclusively in the formation of PhX^- ($\text{X} = \text{O}$ and/or S) from anions $\text{PhX}(\text{CH}_2)_n\text{O}^-$ ($\text{X} = \text{O}$ or S) when $n = 2$.³⁷ The proportion of Smiles rearrangement decreases as n increases. Smiles intermediates are not involved in the formation of products from $\text{PhO}(\text{CH}_2)_n\text{S}^-$ ($n = 2-5$).

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(36) (a) The MS/MS/MS experiment on m/z 94 ($^{12}\text{C}_5^{13}\text{CH}_5\text{O}^-$) shows 95% loss of ^{13}CO . There is a small (5%) component, almost lost in background noise, centered on loss of 28 amu. (b) The MS/MS/MS experiment on m/z 110 ($^{12}\text{C}_5^{13}\text{CH}_5\text{S}^-$) shows a broad peak centered on loss of C_4H_4 . The base of this peak is wide: a small loss (<10%) of $^{13}\text{C}_3^{13}\text{CH}_4$ cannot be excluded on the available data.

(37) A reviewer has asked why condensed-phase Smiles reactions require an additional electron-withdrawing group on the phenyl ring, whereas the gas-phase process does not. Obviously the solvent should reduce the rate of the condensed phase process with respect to the gas-phase reaction, but the precise nature of the solvent in the determination of the rate of the condensed-phase reaction is difficult to quantify. Similarly, published data on intermolecular aryl nucleophilic substitution in the gas phase provides little quantitative information concerning the role of substituents on the overall rates of those reactions [Riveros, J. M.; Jose, S. M.; Takashima, K. In *Advances in Physical Organic Chemistry*; Gold V., Bethell, D., Eds.; Academic Press: London, 1985; Vol. 21, p 234]. We are currently investigating the effects of additional electron-introducing groups on the gas-phase Smiles rearrangement and will shortly report the results of that work.