THEORETICAL STUDIES ON THE GAS-PHASE SMILES REARRANGEMENT*

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Gas-phase Smiles rearrangements and $S_N i$ processes of ions $C_6H_5X(CH_2)_nY^-$ (X, Y = O or S, and $n = 2$–4) have been studied by the AM1 MO method. The Smiles rearrangement to an *ortho* position of the phenyl ring is difficult owing to involvement of a high-energy barrier process involving a 1,2-hydrogen shift. The reactivity of the Smiles rearrangement to the *ipso* position increases in the order X = O and Y = S < X = S and Y = O < X = Y = O as a result of steric and electronic effects in the transition state (TS). The reactivity order with respect to the side-chain length, $n = 3 < 4 < 2$, is mainly determined by ring strain in the TS. For the $S_N i$ process, in which Y attacks the β-carbon (β to phenyl), the enthalpy ($\Delta H^{\neq}$) factor becomes more favourable but the entropy ($\Delta S^{\neq}$) factor becomes unfavourable with an increase in the side-chain length, in agreement with a general trend for cyclization processes. The product ratio in the Smiles rearrangement and the $S_N i$ process is largely controlled by the thermodynamic stabilities of the products, as observed in gas-phase experiments.

INTRODUCTION

The Smiles rearrangement (SR),[2] equation (1), is known to be facilitated by an electron-withdrawing group in either the *ortho* or *para* position on the aromatic ring, and also by a good leaving group X and a strong nucleophile Y.[3] However, possibilities of concomitant intramolecular nucleophilic substitution ($S_N i$) processes, in which Y attacks the β-carbon (β to phenyl), equation (2), and other skeletal rearrangements cannot be precluded.

$$C_6H_5\text{-}X\text{-}(CH_2)_n\text{-}Y^- \rightarrow C_6H_5\text{-}X^- + (CH_2)_n\frown Y$$

(2)
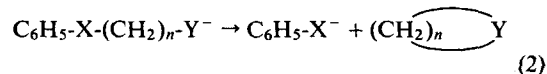
We report here an MO theoretical study of Smiles rearrangement and $S_N i$ processes with X, Y = O or S and $n = 2$–4 [equations (1) and (2)] using the AM1 method.[4] We have also considered the possibility of the SR involving nucleophilic attack on the *ortho* position by Y instead of the normal attack on the *ipso*-carbon resulting in a product with Y substituted at *ortho* to X in the ring, equation (3), and compared the results with those of the gas-phase experiments of Eichinger *et al.*[5]
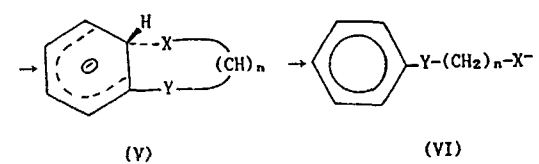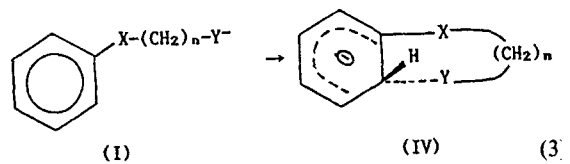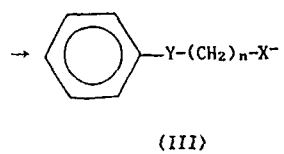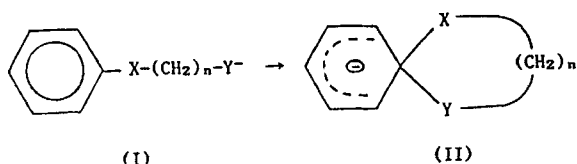
(1)

(3)

COMPUTATIONAL METHOD

The RHF-AM1 procedure[6] was used throughout. Since no biradical or biradicaloid mechanism is expected from equations (1)–(3), the energetics and structure of TSs should be represented adequately by the RHF calculation.[7] Advantages of the AM1 method are twofold: AM1 includes some electron correlation effect through its parameterization, and it requires 2–3 orders of magnitude less computing time than the relatively low-level ab initio method (e.g. 3–21G basis set).[4,7] The latter is especially important in this work because of the relatively complex molecular systems involved (10–12 heavy atoms in I–VI).

It has been shown by Dewar and Yuan[8] that AM1 gives good results for reactions of anionic species, and several studies have been reported indicating that the AM1 method is the best mimic of the ab initio method in the computations of TS geometries.[9] Recently, Reynolds[9] has shown a close correspondence between the AM1 and HF/6–31G* potential surfaces, indicating that AM1 gives geometries for minima and TSs that agree closely with high-level ab initio results. In fact, AM1 is recommended as the most reliable semi-empirical MO method currently available[10]

The ground states (geometries and energies) were fully optimized with respect to all geometric parameters and characterized by the all-positive eigenvalues in the Hessian matrix.[11] End-to-end cyclization TSs were initially approximated and then refined by the gradient norm minimization.[12] The sole negative eigenvalue in the Hessian matrix was confirmed for all the TSs.[11] The activation entropy, $\Delta S^{\ddagger}$, was obtained by subtracting the calculated entropy of the ground state from that of the TS at 423 K, using a program incorporated within the AMPAC.[6]

RESULTS AND DISCUSSION

Reaction mechanisms for $PhO(CH_2)_nO^-$

The n = 2 system.

The potential energy profile of the SR and S_Ni processes for $n = 2$ is presented in Figure 1; the SR process is shown to be more favourable than S_Ni both kinetically and thermodynamically. The TSs given in Figure 2 show that the SR process has a sterically more favourable five-membered cyclic TS whereas the TS for S_Ni involves a three-membered ring which has a high ring strain.[13]

Moreover, the frontier molecular orbital (FMO)[14] interaction in the SR process is also more favourable than in S_Ni, as can be deduced from the FMOs summarized in Table 1; PMO theory[15] requires a smaller FMO energy gap ($\Delta\mathscr{E}_{FMO}$) for a greater reactivity and $\Delta\mathscr{E}_{FMO} = \mathscr{E}_{LUMO} - \mathscr{E}_{HOMO}$ is smaller for SR [LUMO = π^*(ring) = 4·04 eV, HOMO = nonbonding orbital (n) of $-O^- = -3·05$ eV] than for S_Ni [LUMO = σ^*(O—C) = 6·58 eV, HOMO = $n(-O^-)$ = $-3·05$ eV].

In contrast, the comparison of $\Delta S^{\ddagger}$ indicates that the S_Ni process ($\Delta S^{\ddagger} = 5·3$ cal K^{-1} mol^{-1}) is more favourable by $8·9$ cal K^{-1} mol^{-1} compared with SR ($\Delta S^{\ddagger} = -3·6$ cal K^{-1} mol^{-1}) (1 cal = 4·184 J), which is consistent with the general trend of the ring-closure reaction,[16] i.e. a three-membered ring is entropically
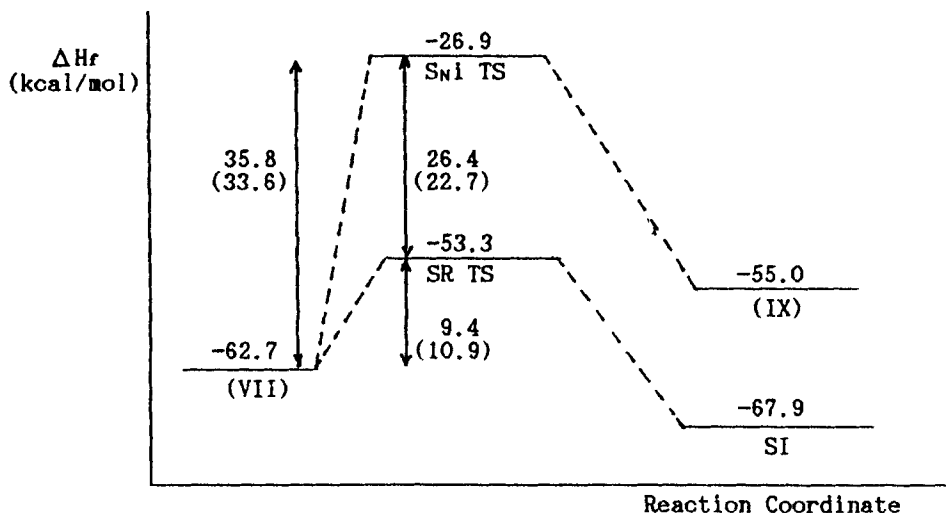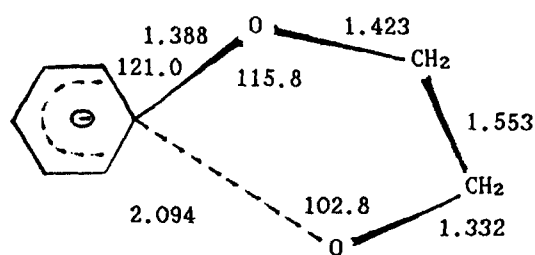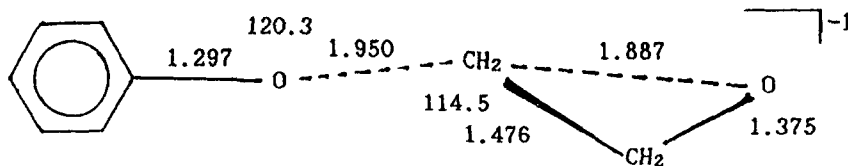

Figure 1. Potential energy profiles for the gas-phase SR and S_Ni processes of $PhO(CH_2)_2O^-$ (**VII**). The $\Delta G^{\ddagger}$ values are in parentheses

(SR TS)

(S$_N$i TS)

Figure 2. TS geometries for the gas-phase SR and S$_N$i processes of PhO(CH$_2$)$_2$O$^-$. Bond lengths and angles are in Å and degrees, respectively

Table 1. FMO energy levels ($\mathscr{E}$) of the ground-state molecules (in eV)

n	FMO	VII (X = Y = O)	XI (X = S, Y = O)	XII (X = O, Y = S)
2	$\mathscr{E}(\pi^*)$	4·04	3·68	4·03
	$\mathscr{E}(\sigma^*)$	6·58	6·61	6·27
	$\mathscr{E}(n)$	−3·05	−3·10	−2·57
3	$\mathscr{E}(\pi^*)$	3·85	3·53	4·02
	$\mathscr{E}(\sigma^*)$	6·18	6·09	6·12
	$\mathscr{E}(n)$	−3·04	−3·08	−2·68
4	$\mathscr{E}(\pi^*)$	3·14	2·83	2·86
	$\mathscr{E}(\sigma^*)$	5·38	5·26	5·04
	$\mathscr{E}(n)$	−2·72	−2·73	−1·96

more favoured than a five-membered ring. However, as can be seen in Figure 1, the contribution of $\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$ ($= \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ at 423 K) is not large enough for the S$_N$i process to reverse the reactivity trend based on $\Delta H^{\ddagger}$ in favour of S$_N$i when the reactivity is compared in terms of $\Delta G^{\ddagger}$.

According to Eichinger et al.,[5] gas-phase experiments involving isotope labelling with ^{18}O for X = O gave the product ratio PhO$^-$: Ph^{18}O$^-$ = 50 : 50. This result can be rationalized if a pre-equilibrium exists between VII and VIII through an
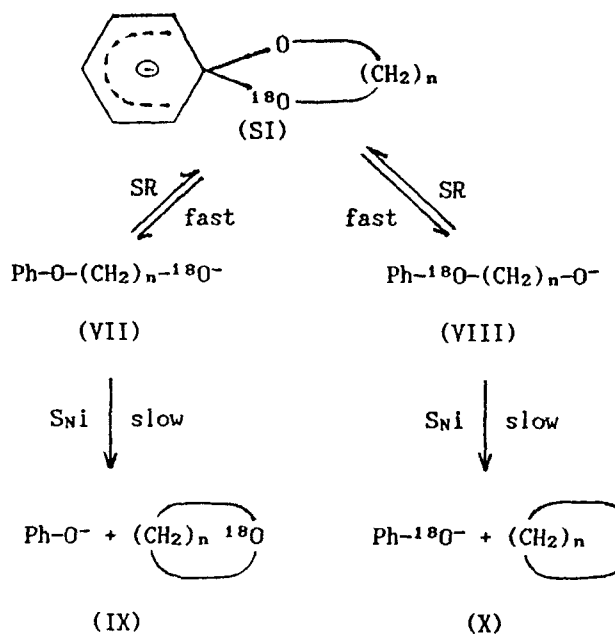
Scheme 1

intermediate (SI), i.e. if the two processes VII → VIII and VIII → VII are very fast compared with the $S_N i$ processes leading to IX and X in Scheme 1; the abundances of species VII and VIII will then become equal and hence the amounts of the products, IX and X, will become the same. Reference to Figure 1 reveals that there is a $\Delta G^{\neq}$ difference of 22·7 kcal mol^{-1} between the SR ($\Delta G^{\neq} = 10\cdot9$ kcal mol^{-1}) and $S_N i$ ($\Delta G^{\neq} = 33\cdot6$ kcal mol^{-1}) processes. This difference is certainly sufficient to establish the pre-equilibrium between the two isotopically different reactants, VII and VIII, and will result in a product ratio IX : X = 50 : 50, in agreement with the experiments.

The n = *3 system*

The $n = 3$ system gives essentially the same reactivity pattern as the $n = 2$ system above. The TS structures in Figure 3 show that the SR process has a six-membered cyclic TS whereas the TS for $S_N i$ includes a four-membered cyclic structure which is equally strained sterically as a three-membered ring in the $n = 2$ case above; thus the SR process is energetically ($\Delta H^{\neq}$) more favoured than $S_N i$. The FMO gap, $\Delta\mathscr{E}_{FMO}$, is narrower by 2·3 eV (Table 1) and hence the SR reactivity will be higher on the electronic ground also.

In contrast, the entropy factor is more favourable for

the $S_N i$ process ($\Delta S^{\neq} = 2\cdot9$ cal K^{-1} mol^{-1}) than for SR ($\Delta S^{\neq} = -3\cdot6$ cal K^{-1} mol^{-1}). Nevertheless, the overall reactivity of the SR process based on $\Delta G^{\neq}$ is still higher than $S_N i$ by 13·9 kcal mol^{-1}, as shown in Figure 4. This gap in $\Delta G^{\neq}$ [$\delta\Delta G^{\neq} = \Delta G^{\neq}(S_N i) - \Delta G^{\neq}(SR)$] is higher by 8·8 kcal mol^{-1}, and hence the preference of the SR to $S_N i$ is greater for the $n = 2$ than for the $n = 3$ system, which is mainly due to the $\Delta G^{\neq}$ difference for the SR process between $n = 2$ and 3 in favour of the former, i.e. $\Delta G^{\neq}_{SR}(n = 3) - \Delta G^{\neq}_{SR}(n = 2) = 18\cdot4 - 10\cdot9 = 7\cdot5$ kcal mol^{-1}.

This relatively higher energy barrier of the SR process for $n = 3$ than for $n = 2$ can be attributed to two factors. (i) Kinetically, the formation of a five-membered ring ($n = 2$) is known to be more facile than that of a six-membered ring ($n = 3$) in intramolecular cyclization processes.[17] Especially when the attacking nucleophile has more than two lone pairs, as in this case with an oxygen atom, stereoelectronic effects in the TS favour the five-membered rather than the six-membered cyclization.[18] (ii) Thermodynamically, the stability of the six-membered intermediate, SI (II with $n = 3$), is less than that of the five-membered intermediate, SI (II with $n = 2$), owing to a greater ring strain. For a typical cycloalkane system, a six-membered ring is less strained than a five-membered ring, but in the SI, II, two oxygen atoms are situated at a *gem*-site to each other within the cyclic system; thus, in contrast to a normal cycloalkane
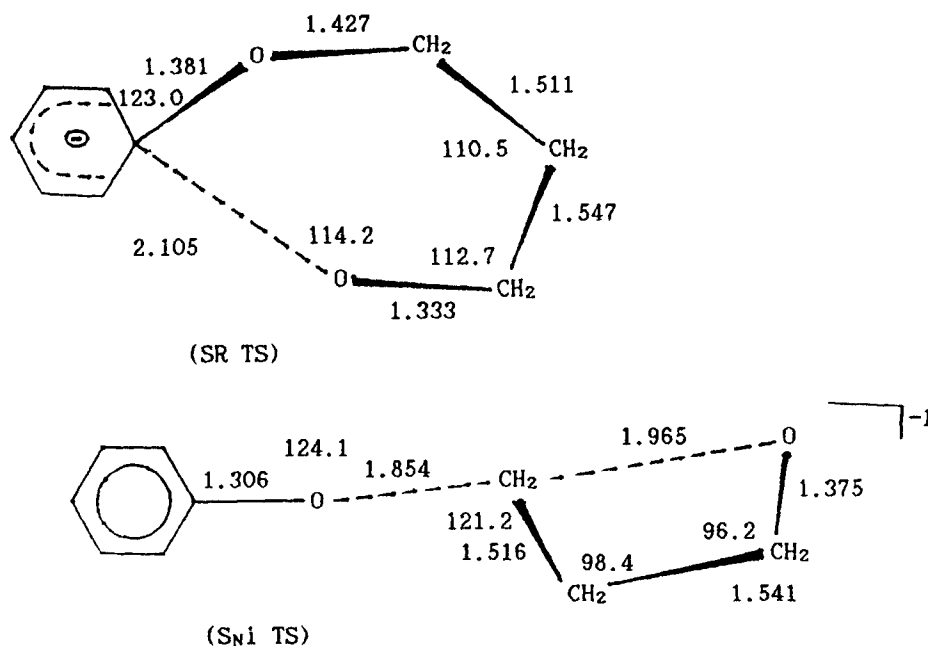

(SR TS)

(S$_N$i TS)

Figure 3. TS geometries for the gas-phase SR and $S_N i$ processes of PhO(CH$_2$)$_3$O$^-$. Bond lengths and angles are in Å and degrees, respectively

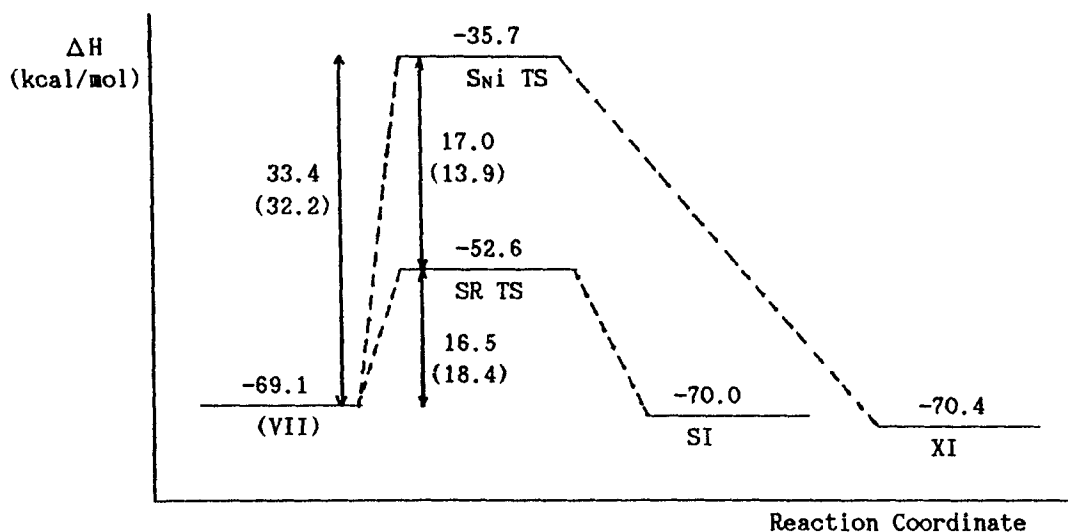Figure 4. Potential energy profiles for the gas-phase SR and $S_N i$ processes of $PhO(CH_2)_3O^-$ (**VII**). The $\Delta G^{\ddagger}$ values are in parentheses

system, the five-membered SI ($n = 2$) has less ring strain than the six-membered SI ($n = 3$).

This type of atypical ring strain for the SI, **II**, can be demonstrated by comparing the heats of formation (ΔH_f) of the reactants and SIs for $n = 2$ and 3: for $n = 2$, $\delta \Delta H_f = \Delta H_f(\text{SI}) - \Delta H_f(\text{reactant}) = 5 \cdot 2$ kcal mol^{-1}, whereas for $n = 3$, $\delta \Delta H_f = 0 \cdot 9$ kcal mol^{-1}, indicating the relative instability of the SI for $n = 3$ compared with that for $n = 2$. The relatively higher ring strain in the intermediate will, of course, result in a higher partial ring strain in the TS (for $n = 3$) for the formation step of the intermediate.

The experimental product ratio $PhO^- : Ph^{18}O^- = 100 : 76$ for the $n = 3$ system by Eichinger et al.[5] can easily be accommodated with the above arguments. Although, the SR process is more favourable than $S_N i$ for the $n = 3$ system, as it is for $n = 2$, the energy gap in $\Delta G^{\ddagger}$ [$\delta \Delta G^{\ddagger} = \Delta G^{\ddagger}(S_N i) - \Delta G^{\ddagger}(\text{SR})$] is considerably smaller for $n = 3$ than for $n = 2$; hence the $S_N i$ process for $n = 3$, **VII** → **IX** in Scheme 1, becomes more competitive with the SR process, **VII** ⇌ **VIII**, unlike for the $n = 2$ system, so that a greater product ratio in favour of PhO^- is obtained.

The n = *4 system*

In this case, the $S_N i$ process has a less strained structure of the five-membered cyclic TS, as shown in Figure 5. The energy barrier for this process, $\Delta G^{\ddagger} = 18 \cdot 1$ kcal mol^{-1}, is lower by 14–15 kcal mol^{-1} than the corresponding processes for the $n = 2$ and 3 systems. However, the $\Delta G^{\ddagger}$ value for the SR process

is $15 \cdot 2$ kcal mol^{-1}, which is lower by $2 \cdot 9$ kcal mol^{-1} than that for the $S_N i$ process (Figure 6); the two TSs for SR and $S_N i$ have seven- and five-membered ring structures, respectively, so that not very different degrees of partial ring strain are involved. Here again the FMO gap is narrower for SR ($\Delta \mathcal{E}_{\text{FMO}} = 5 \cdot 86$ eV) than for $S_N i$ ($\Delta \mathcal{E}_{\text{FMO}} = 8 \cdot 10$ eV), and hence SR is favoured electronically as it is for $n = 2$ and 3, but the products from $S_N i$ are more stable than those from SR, in contrast to the $n = 2$ and 3 systems for which the opposite applied. This difference in product stabilities is expected to change the trend in the product ratio.

According to the gas-phase experimental results of Eichinger et al.[5] with $Y = {}^{18}O$, only PhO^- is obtained as the product for $n = 4$, indicating that the $S_N i$ process, **VII** → **IX**, is much more favourable than the SR process, **VII** → **VIII**, in Scheme 1. The energy profile in Figure 6 shows that $\Delta G^{\ddagger}$ for SR (**VII** ⇌ SI) is lower only by $2 \cdot 9$ kcal mol^{-1} than that for $S_N i$ of **VII** → **IX**, so that the two processes may compete. Moreover, the SI, once formed, will be thermalized before proceeding to either **VIII** or back to **VII**. This latter SR process, SI → **VIII**, has a higher activation barrier by $0 \cdot 8$ kcal mol^{-1} than the $S_N i$ process, **VII** → **IX**, and the products in this $S_n i$ process are much more stable than the SI [$\delta \Delta H_f = \Delta H_f(\text{SI}) - \Delta H_f(\text{product}) \approx 29$ kcal mol^{-1}]. Hence the $S_N i$ process of **VII** → **IX** is both kinetically and thermodynamically preferred to the SR process; hence the product will be mainly PhO^- that is produced in the $S_N i$ process of **VII** → **IX**, in satisfactory agreement with the experimental results.
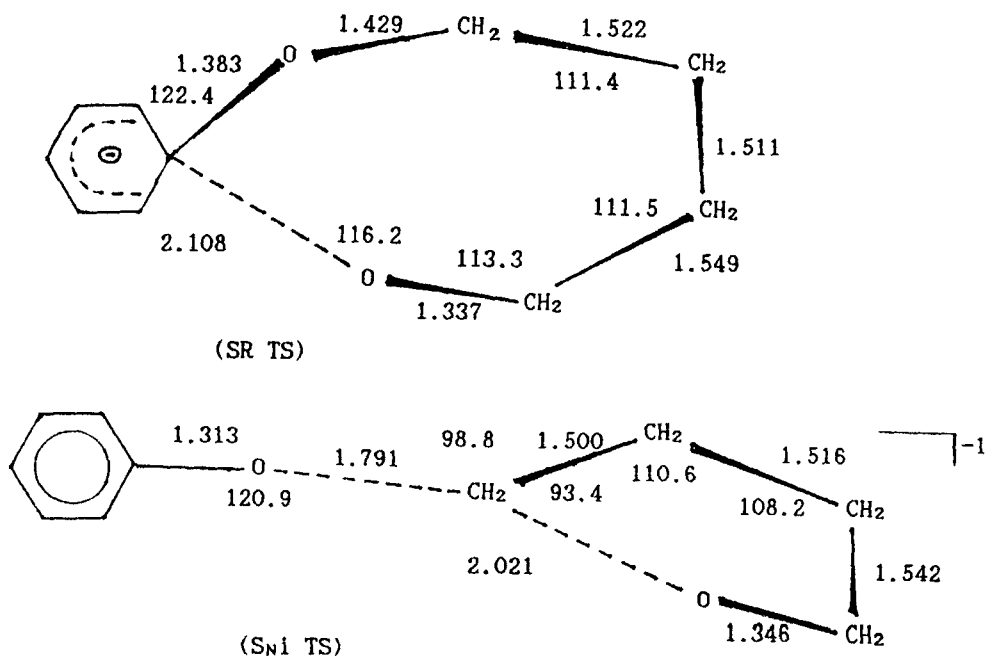
Figure 5. TS geometries for the gas-phase SR and $S_N i$ processes of $PhO(CH_2)_4O^-$ Bond lengths and angles are in Å and degrees, respectively
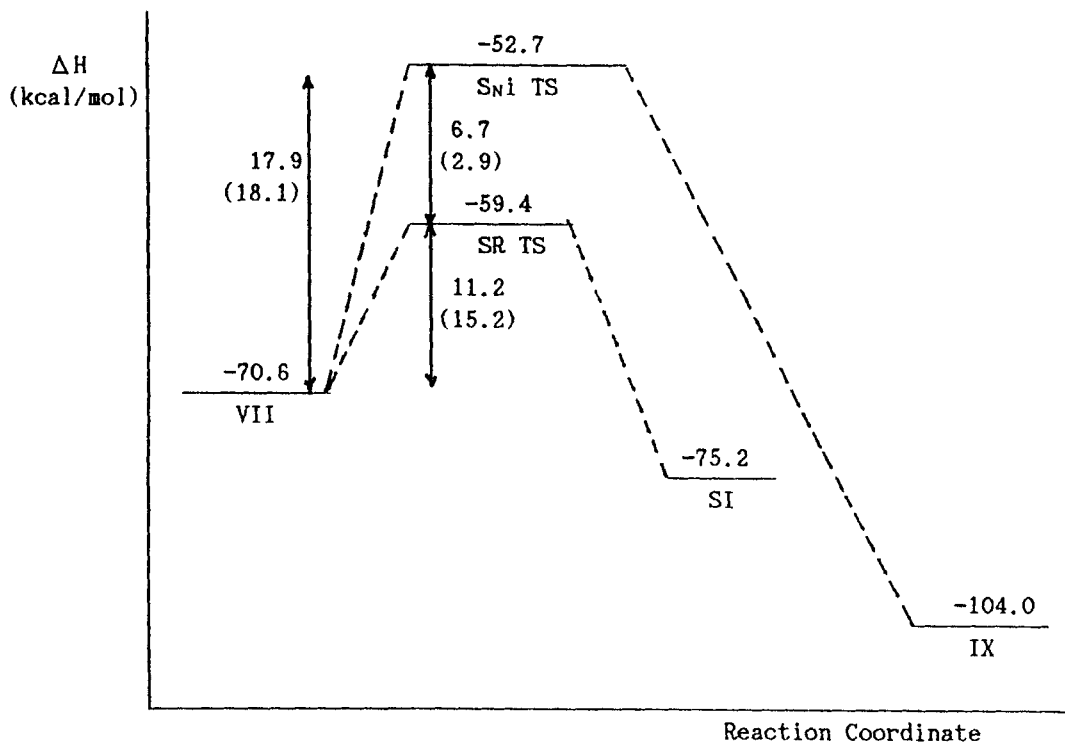

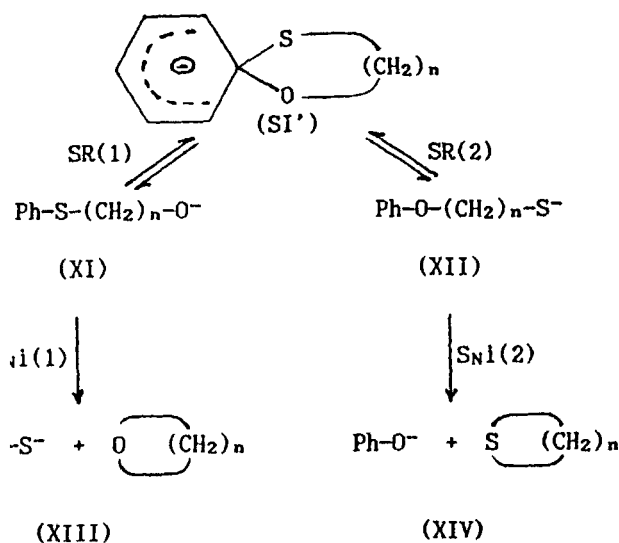Figure 6. Potential energy profiles for the gas-phase SR and $S_N i$ processes of $PhO(CH_2)_4O^-$ (VII). The $\Delta G^{\ddagger}$ values are in parentheses

Reaction mechanism for $PhS(CH_2)_nO^-$ (XI) and $PhO(CH_2)_nS^-$ (XII)

Conceivable reaction pathways for anions XI and XII are shown in Scheme 2. Anions XI and XII are interchangeable through two SR processes. This means that a pre-equilibrium can be set up between XI and XII if the SR processes are very much favoured compared with the two S_Ni processes from XI and XII, and the product ratio of XIII to XIV will depend on the relative abundance of XI and XII and the relative reactivity of the two S_Ni processes.

Scheme 2

The n = 2 system

The potential energy profile for this system in Figure 7 shows that the $\Delta G^{\pm}$ values for the two SR processes, SR(1) and SR(2), are lower by 11·3 and 16·1 kcal mol^{-1}, respectively, than the corresponding S_Ni processes, suggesting that a pre-equilibrium between XI and XII is possible. However, the stability of XII is slightly greater (by $\Delta H_f = 1·0$ kcal mol^{-1}) than that of X, and hence a slightly larger amount of XII can be expected. Here again the SR processes from XI and XII are more favoured than S_Ni owing to less ring strain in the TS and a narrower inter-frontier level gap, $\Delta \mathscr{E}_{FMO}$, just as was seen above for the X = Y = O derivative with $n = 2$.

For the X = S and Y = O compound, XI, the barrier height $(\Delta G^{\pm})$ for the S_Ni process (34·5 kcal mol^{-1}) is similar to that for S_Ni from VII (33·6 kcal mol^{-1}) of the X = Y = O derivative. Reference to Figures 2 and 8 and Table 1 reveals that the steric and electronic effects $(\Delta \mathscr{E}_{FM})$ are very similar in the two S_Ni processes.

However, the SR process from XI is less favourable (by $\Delta G^{\pm} = 7·5$ kcal mol^{-1}) than that from VII, despite the similar electronic effect $(\Delta \mathscr{E}_{FMO})$ for the two cases. The reason for the less favourable $\Delta G^{\pm}$ value for SR from XI may be found in Table 2, where it is seen that the charge density (q) of the *ipso*-carbon (C-1) in XI is $-0·174$ whereas it is $+0·118$ in VII, owing to the difference in the electronegativity between X = S (XI) and X = O (VII). As a result, the electrostatic interaction,[19] $\mathscr{E}_{es}$, in the SR process from VII will be more favourable than that from XI giving a lower $\Delta G^{\pm}$ value.

The contribution of $\mathscr{E}_{es}$ toward the SR process is also consistent with the enhanced reactivity found in the condensed-phase experiment when an electron-withdrawing group is substituted in either the *ortho* or *para* position on the aromatic ring,[2,3] since such a group confers on the *ipso*-carbon (C-1) a greater positive charge, permitting a more facile nucleophilic attack by Y. Another disadvantage for XI in the SR process is that the sulphur atom (X = S) has a bulky van der Waals radius with a greater steric repulsion between X and Y in the cyclic TS compared with the oxygen atom (X = O) in VII. Formation of SI' is therefore an endothermic process, $\delta \Delta H_f = \Delta H_f(SI') - \Delta H_f(XI) = 3·7$ kcal mol^{-1}, the steric effect playing a major role, in contrast to exothermic formation of the intermediate from VII, SI, $\delta \Delta H_f = \Delta H_f(SI) - \Delta H_f(VII) = -5·2$ kcal mol^{-1}.

For the compound with X = O and Y = S, XII, the S_Ni process has lower energy barrier $(\Delta G^{\pm} = 24·2$ kcal mol^{-1}) than that for VII $(\Delta G^{\pm} = 33·6$ kcal mol^{-1}) and XI $(\Delta G^{\pm} = 34·4$ kcal mol^{-1}); no doubt the ring strain involved in the three-membered cyclic TS should be similar in the three cases, but the electronic effect $(n-\sigma^*$ interaction) favours XII owing to a narrower FMO energy gap (Table 3). On the other hand, for the SR process, the barrier height increases in the order VII < XII < XI, which should be the overall result of various contributing effects; Table 3 reveals that for XII the electronic interaction $(\Delta \mathscr{E}_{FMO})$ will be most favourable as noted above, but facility of the nucleophilic attack by Y (q_{ipso}) should be medium between VII and XI. When these are considered together with a relatively large steric effect for XI and XII due to the involvement of an S atom in the TS, the reactivity order based on $\Delta G^{\pm}$ above seems reasonable. The energetics summarized in Figure 7 can be used to compare our AM1 results with the gas-phase experimental results of Eichinger *et al.*[5] They reported a product ratio PhO$^-$: PhS$^-$ = 100 : 57 for the reaction of XI. This product ratio suggests that the SR processes are very facile compared with the S_Ni processes, in Scheme 2, so that there is a pre-equilibrium set up between XI and XII, and also the $S_Ni(2)$ process, XII → XIV, has a relatively lower activation barrier

ΔH_f
(kcal/mol)

36.3
(34.5)
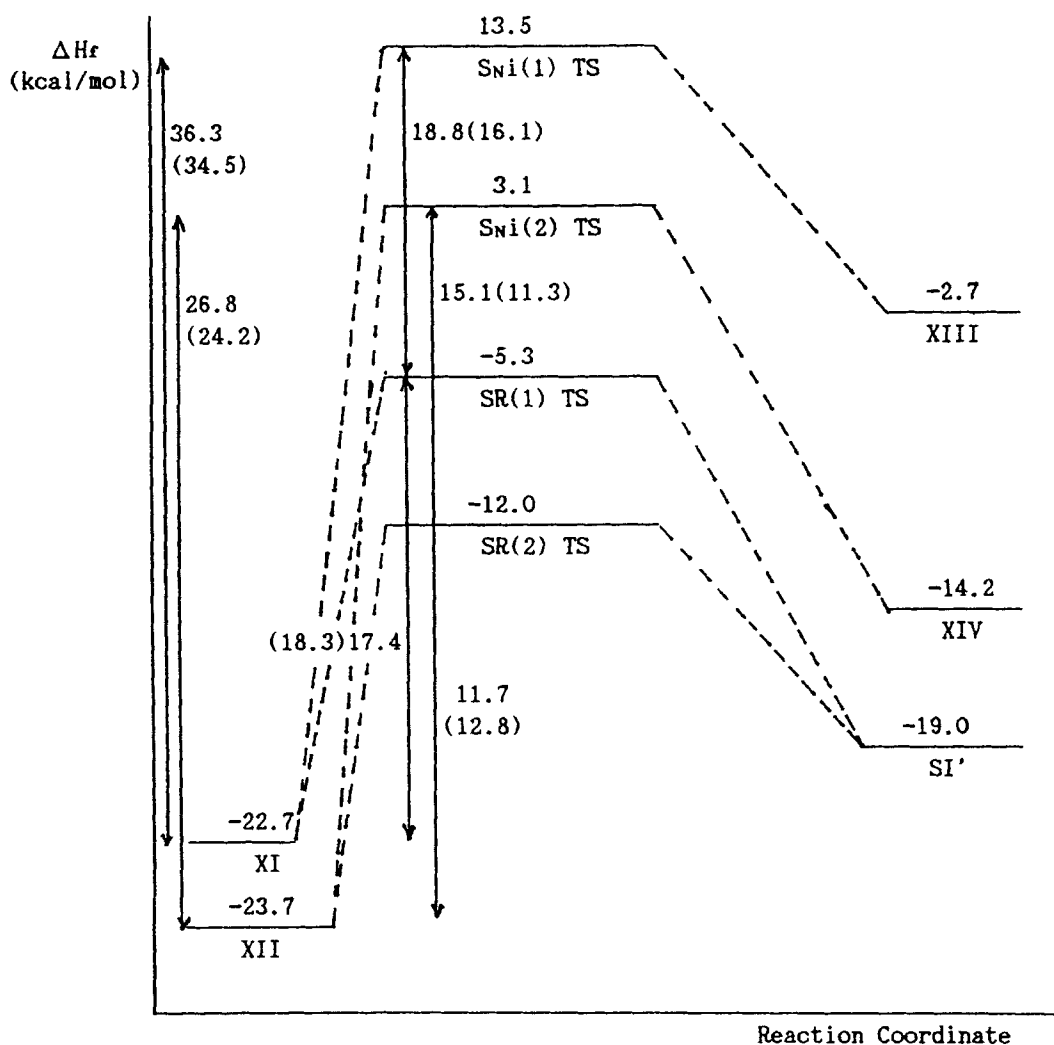
26.8
(24.2)

13.5
$S_Ni(1)$ TS

18.8(16.1)

3.1
$S_Ni(2)$ TS

15.1(11.3)

-5.3
SR(1) TS

-12.0
SR(2) TS

-2.7
XIII

-14.2
XIV

-19.0
SI'

(18.3)17.4

11.7
(12.8)

-22.7
XI

-23.7
XII

Reaction Coordinate

Figure 7. Potential energy profiles for the gas-phase SR and S_Ni processes of $PhS(CH_2)_2O^-$ (**XI**) and $PhO(CH_2)_2S^-$ (**XII**). The $\Delta G^{\ddagger}$ values are in parentheses

than the $S_Ni(1)$ process, **XI → XIII**. This is indeed what we obtained by the AM1 calculations as summarized in Figure 7.

On the other hand, the sole product observed experimentally from **XII** was reported to be PhO^-.[5] This can also be explained by our AM1 theoretical results in Figure 7. We note that process **XII → SI'** is the most facile, but the process **SI' → XI** is unfavourable compared with the equilibrium **SI' ⇌ XII**. Further, even if **XI** is formed by the SR processes, the $S_Ni(1)$ process, **XI → XIII**, leading to the product PhS^- is unfavourable both kinetically and thermodynamically compared with the $S_Ni(2)$ process,
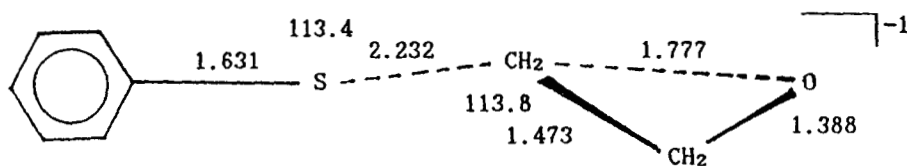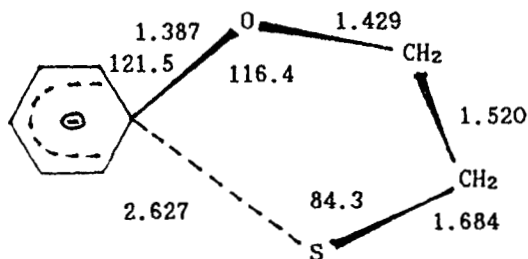
XII → XIV, so that only the product PhO^- is to be expected as observed in the gas-phase experiments.

Table 2. Charge density (q) of the *ipso*-carbon (C-1) of the phenyl ring (in electronic charge units)

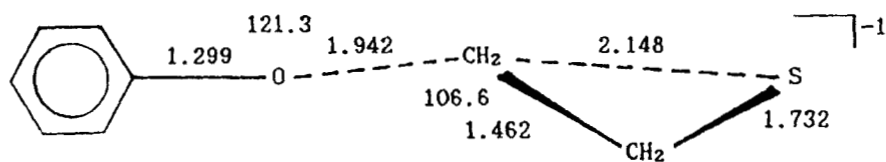| n	VII (X = Y = O)	XI (X = S, Y = O)	XII (X = O, Y = S)
2	0.118	−0.174	0.086
3	0.096	−0.186	0.076
4	0.097	−0.187	0.095
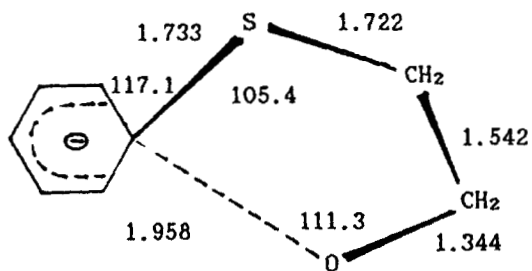
Figure 8. TS geometries for the gas-phase SR and S_{Ni} processes of $PhS(CH_2)_2O^-$ and $PhO(CH_2)_2S^-$. Bond lengths and angles are in Å and degrees, respectively

Table 3. Comparison of relevant data for the SR reactivity of the three reactants with $n = 2$

Parameter	VII (X = Y = O)	XI (X = S, Y = O)	XII (X = O, Y = S)
$\Delta G^{\ddagger}$ (kcal mol^{-1})	10·9	18·3	12·8
$\Delta \mathscr{E}_{FMO}$ (eV)	9·63	9·71	8·84
q_{ipso} (electronic charge unit)	+0·118	−0·174	+0·086
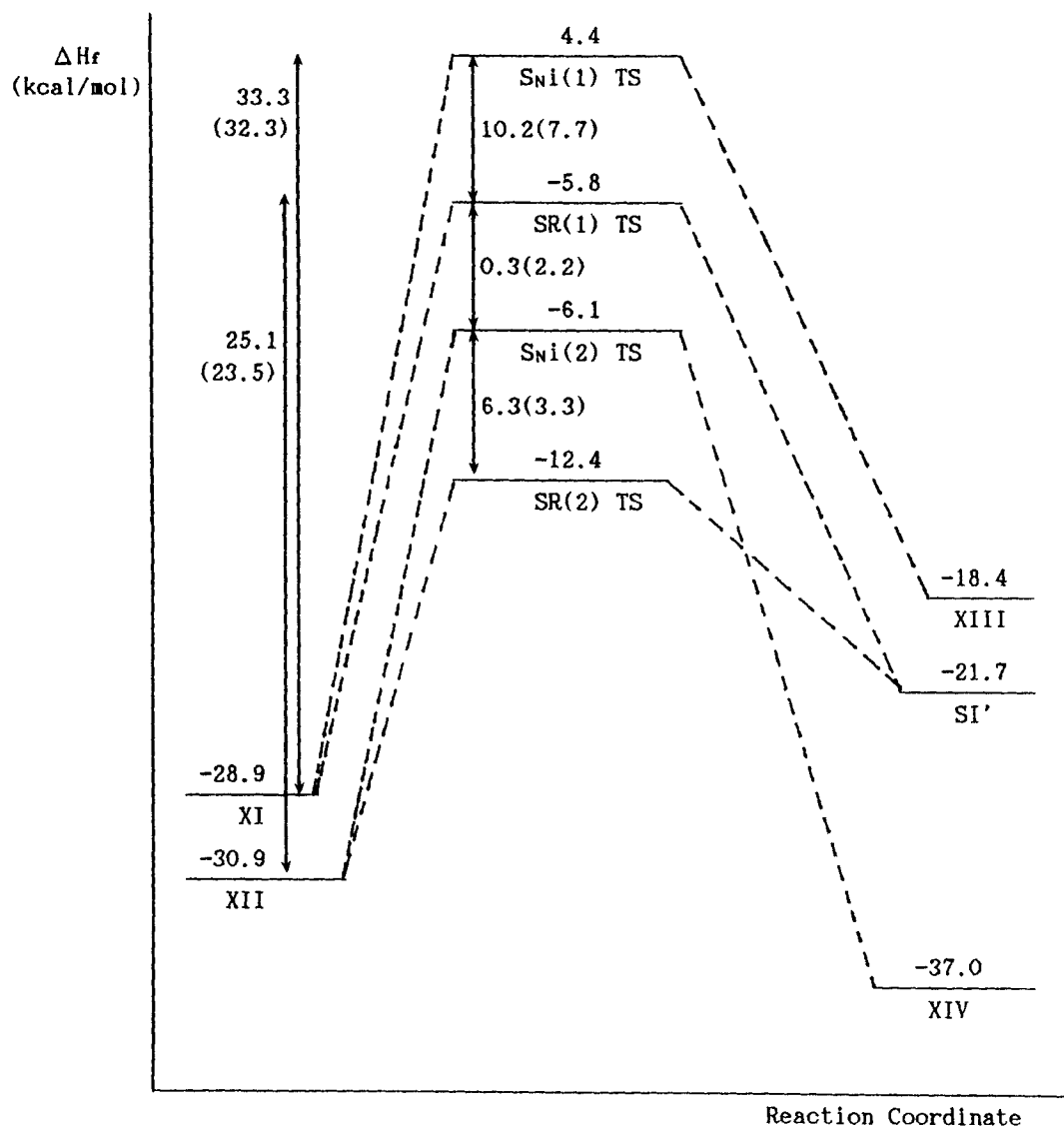
Figure 9. Potential energy profiles for the gas-phase SR and $S_N i$ processes of PhS(CH$_2$)$_3$O$^-$ (XI) and PhO(CH$_2$)$_3$S$^-$ (XII). The $\Delta G^{\ddagger}$ values are in parentheses
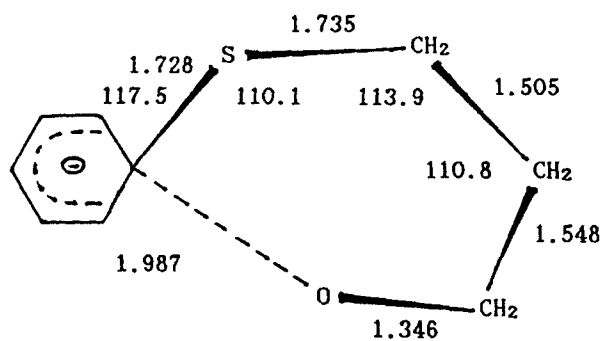
Figure 10. TS geometries for the gas-phase SR and S_Ni processes of $PhS(CH_2)_3O^-$ and $PhO(CH_2)_3S^-$. Bond lengths and angle are in Å and degrees, respectively
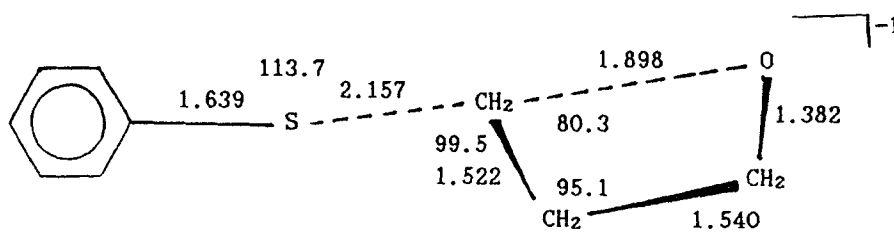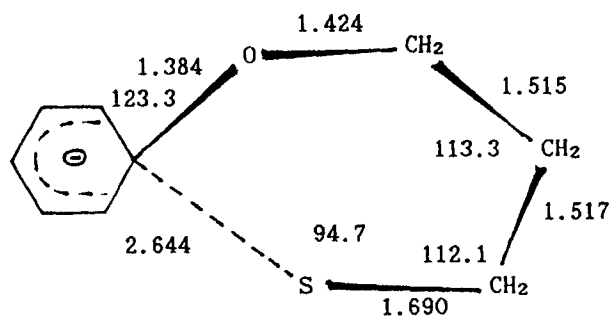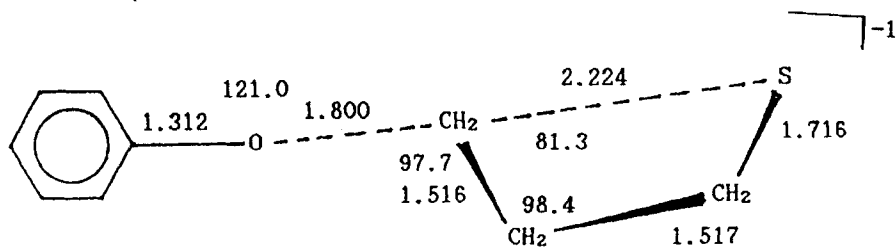
The n = *3 system*

The potential energy profile in Figure 9 shows that the reactivity trend will be similar to that of the $n = 2$ system. The product ratio from the gas-phase experiments is, however, $PhO^- : PhS^- = 100 : 36$ ($100 : 57$ for $n = 2$) for this system. A small relative decrease in the product PhS^- can be explained by the energetics for various reaction paths shown in Figure 9. The differences in the heats of formation between **XI** and **XII** are $\delta\Delta H_f = \Delta H_f(\mathbf{XI}) - \Delta H_f(\mathbf{XII}) = 1\cdot0$ and $2\cdot0$ kcal mol^{-1} for the $n = 2$ and 3 systems, respectively,

so that a larger relative population of **XII** through SR processes $\mathbf{XI} \rightleftharpoons \mathbf{XII}$ is to be expected for $n = 3$. Moreover, for $n = 3$ the $S_N i(2)$ process, $\mathbf{XII} \rightleftharpoons \mathbf{XIV}$, has a lower barrier by $(\Delta G^{\pm} =)$ $2\cdot2$ kcal mol^{-1} than the SR process of $\mathbf{XII} \rightarrow \mathbf{SI'} \rightarrow \mathbf{XI}$, so that $S_N i(2)$, $\mathbf{XII} \rightarrow \mathbf{XIV}$, becomes relatively more favourable than $S_N i(1)$, $\mathbf{XI} \rightarrow \mathbf{XIII}$, when compared with the corresponding processes for the $n = 2$ system. This will naturally give a larger relatively yield of PhO^- for $n = 3$ than $n = 2$. On the other hand, PhO^- is reported to be the sole product from **XII** through the $S_N i(2)$ process, $\mathbf{XII} \rightarrow \mathbf{XIV}$, which is similar to the results for the $n = 2$
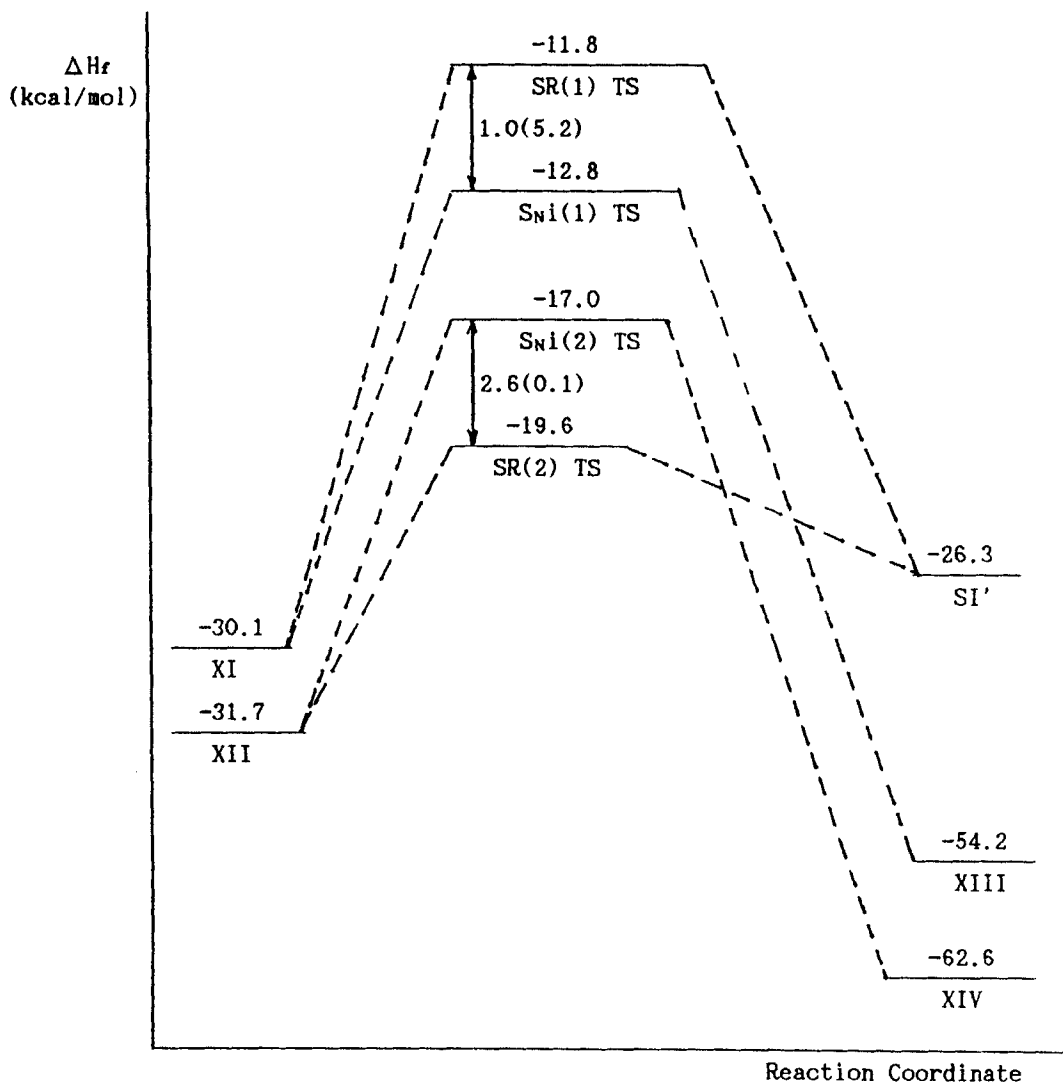

Figure 11. Potential energy profiles for the gas-phase SR and $S_N i$ processes of $PhS(CH_2)_4O^-$ (**XI**) and $PhO(CH_2)_4S^-$ (**XII**). The $\Delta G^{\pm}$ values are in parentheses
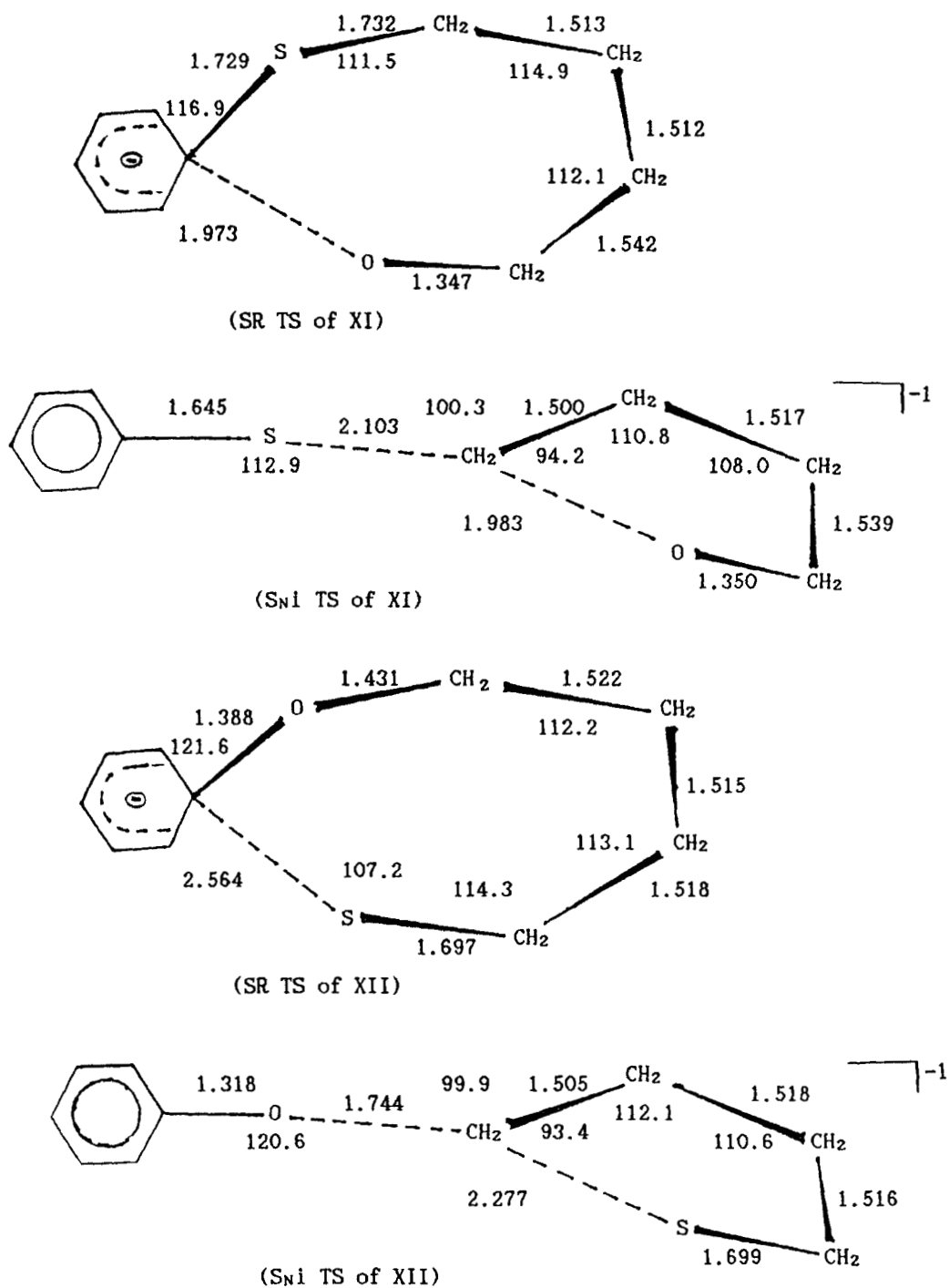
Figure 12. TS geometries for the gas-phase SR and S_{Ni} processes of $PhS(CH_2)_4O^-$ and $PhO(CH_2)_4S^-$. Bond lengths and angles are in Å and degrees, respectively

system. The potential energy profile in Figure 9 is in agreement with this experimental result, as we have discussed in detail above for the $n = 2$ case. The TS structures involved in the reactions of the $n = 3$ system are presented in Figure 10.

The n = 4 system

Finally, the potential energy profile for the $n = 4$ system in Figure 11 shows that the SR process of **XI** has a higher $\Delta H^{\ddagger}$ value by $1 \cdot 0\ \mathrm{kcal\,mol^{-1}}$ than the $S_N i$ process, which, considered together with the more unfavourable $\Delta S^{\ddagger}$ value for SR, rises to an even higher barrier height difference of $(\Delta G^{\ddagger} =)$ $5 \cdot 2\ \mathrm{kcal\,mol^{-1}}$. Hence, unlike any other reactants discussed above, the $S_N i$ process is favoured relative to SR for **XI** with $n = 4$. This unusual trend can be rationalized by a larger steric effect in the TS for the SR than that for the $S_N i$ process, other factors, $\Delta\mathscr{E}_{\mathrm{FMO}}$ and q_{ipso}, pointing to a general reactivity trend favouring the SR process. The TS geometries presented in Figure 12 indicate that the SR TS includes a bulky S atom in a seven-membered cyclic structure, whereas in the $S_N i$ TS no S atom is involved in a relatively stable five-membered cyclic structure. Since $S_N i$ has a lower activation barrier than SR, the $S_N i(1)$ process, **XI** → **XIII**, can now compete with the SR processes, **XI** ⇌ **XII**, with no possibility of a pre-equilibrium between **XI** and **XII** in Scheme 2. This means that the product ratio PhO$^-$: PhS$^-$ will follow the Hammett–Curtin principle[20] so that the relative activation barrier of the two processes will determine the product ratio. Hence the AM1 reactivity trend in favour of $S_N i(1)$ (leading to PhS$^-$) rather than SR(1) (leading to PhO$^-$) is in line with the gas-phase product ratio PhO$^-$: PhS$^-$ = 4 : 100.

On the other hand, for **XII** the two processes, SR(2) (**XII** → SI$'$) and $S_N i(2)$ (**XII** → **XIV**), have similar barrier heights, $\delta\Delta G^{\ddagger} = \Delta G^{\ddagger}\,[S_N i(2)] - \Delta G^{\ddagger}\,[(SR(2)] = 0 \cdot 1\ \mathrm{kcal\,mol^{-1}}$, and hence the two processes will proceed with similar reactivity. However, the two steps in the process SI$'$ → **XI** → **XIII** leading to the product PhS$^-$ are both unfavourable compared with the $S_N i(2)$ process (**XII** → **XIV**) leading to PhO$^-$. This is again consistent with the sole product PhO$^-$ found in the gas-phase experiment from **XII** with $n = 4$.

Possibility of the Smiles rearrangement (SR) to the ortho position

Condensed-phase SR reaction is known to proceed by a nucleophilic attack of Y at the *ipso* position (C-1) of the X-substituted phenyl ring. However, we shall also consider the possibility of Y attacking at the *ortho* position (C-2 or C-6) as in equation (3). The normal SR reaction at the *ipso*-carbon has been shown to proceed by a two-step mechanism through an intermediate, SI; in con-

Table 4. Heats of formation (ΔH_f in kcal mol^{-1}) of the species **IV** and TSs involved in processes **I** → **IV** and **IV** → **V** for the $n = 2$ system in equation (3)

I	**IV**	TS	
		I → **IV**	**IV** → **V**
X = Y = O	$-62 \cdot 1$	$-47 \cdot 1$	$4 \cdot 9$
X = S, Y = O	$-25 \cdot 8$	$-9 \cdot 9$	$39 \cdot 7$
X = O, Y = S	$-22 \cdot 6$	$-13 \cdot 4$	$39 \cdot 7$

trast, the SR process at the *ortho* position, equation (3), needs three steps requiring a 1,2-hydrogen-transfer process between intermediates **IV** and **V**. The heats of formation, ΔH_f, are given in Table 4 for the species **IV** and the TSs for processes **I** → **IV** and **IV** → **V** with $n = 2$. Reference to Table 4 reveals that the ΔH_f values for species **IV** and the process **I** → **IV** are similar to those for the corresponding SI and TSs in the normal SR processes at the *ipso*-carbon, but the 1,2-hydrogen-transfer process, **IV** → **V**, is seen to be extremely unfavourable. This suggests that the SR at the *ortho* position can not occur, in agreement with the condensed-phase[2,3] and the gas-phase experimental results.[5] The heats of formation data for the $n = 3$ and 4 systems are similar to those for $n = 2$.

In all cases the first step in equation (3), i.e. the nucleophilic attack of Y at the *ortho* position, can occur similarly with the attack at the *ipso* position; it is the second step, the 1,2-hydrogen transfer, that prevents the reaction, equation (3), from taking place.

We conclude that (i) for the anions with X = Y = O the SR is more favourable than the $S_N i$ process, but the energy difference, $\delta\Delta G^{\ddagger}$, between the two processes decreases, eventually reversing the reactivity trend in favour of $S_N i$ as the chain length grows from $n = 2$ to 4; (ii) the anions with X = S and Y = O have similar reactivity trends to those with X = Y = O; (iii) for the anions with X = O and Y = S the $S_N i$ process is always more favoured irrespective of n, in contrast to the above two cases; and (iv) the SR process normally occurs at the *ipso* position, the possibility of the process occurring at the *ortho* position being small owing to a 1,2-hydrogen shift. All these results are in good agreement with the gas-phase experimental results.

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