Collision-Induced Elimination of Alkenes from Deprotonated Unsaturated Ethers in the Gas Phase. Reactions Involving Specific β-Proton Transfer

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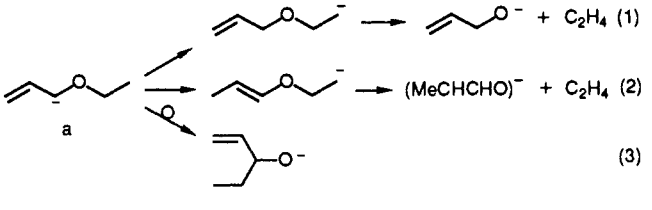
Abstract: Unsaturated ethers $CH_2{=}CHCH_2(CH_2)_nOR$ deprotonate in the gas phase to form $CH_2{=}C\bar{C}H(CH_2)_nOR$. When R ≥ Et it was anticipated that collisional activation should cause β-proton transfer to the carbanion site to form the E1cB intermediate $CH_2{=}CH(CH_2)_{n+1}OCH_2CH_2^-$ (R = Et), which should then eliminate ethene to yield the alkoxide $CH_2{=}CH(CH_2)_{n+1}O^-$. This is the predominant reaction when n = 1 and 2 but diminishes in importance as the value of n increases. When n = 0, the β-proton transfer occurs to the methine position on the double bond, yielding deprotonated acetone as the product anion. Evidence is presented that suggests the following mechanism: $CH_2{=}C\bar{C}HOEt \xrightarrow{-C_2H_4} {}^-CH_2CH_2CHO \rightarrow \overline{CH_2CH_2CHO}^- \rightarrow (MeCOCH_2)^-$.

Nucleophilic substitution and elimination reactions are perhaps the most studied processes in solution,[1] and the two reactions are often competitive. While S_N2 reactions have been extensively studied in the gas phase,[2] elimination reactions have received less attention.[3-7] The current opinion is that strong-base-induced gas-phase elimination reactions are likely to follow an E1cB mechanism (Scheme I) rather than the concerted E2 process, unless the particular E1cB intermediate is energetically inaccessible.

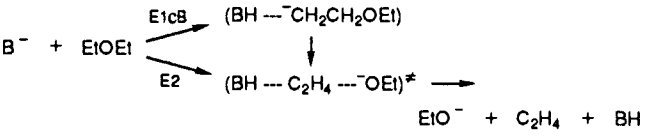
Moreover, in the majority of studies of gas-phase elimination reactions, a strong base and, for example, a dialkyl ether undergo a bimolecular reaction to directly yield the alkoxide ion RO^- by elimination.[4-6] In a different approach, Nibbering[7] has formed a deprotonated thioether, which, if generated in a highly exothermic ion–molecule reaction, subsequently undergoes proton transfer and elimination as shown in Scheme II.

We wished to undertake a similar investigation of ethers; i.e., we wished to indirectly form the E1cB intermediate by proton transfer from some suitable carbanion. However, simple dialkyl ethers do not readily form stable deprotonated species with strong bases, since (i) they are very weak acids (e.g., $\Delta H°_{acid}(Me_2O)$ = 407 kcal mol^{-1})[8] and (ii) the negative ion may be unstable with respect to its radical.[8] So we must adopt a different strategy. We have recently summarized the major collision-induced fragmentation pathways of even-electron negative ions: if direct fragmentation of the initially formed carbanion cannot be effected, proton-transfer reactions and/or skeletal rearrangement processes will precede fragmentation.[9]

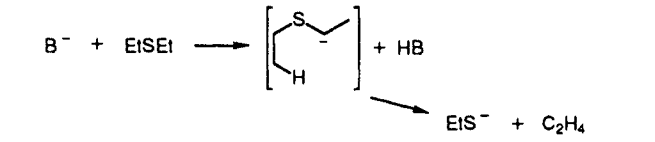
An allyl alkyl ether should deprotonate to form the stable species a; this could, on collisional activation, undergo proton transfer to the carbanion site followed by elimination of ethene to form the allyloxy anion (eq 1) or proton transfer to the terminal methylene group to produce deprotonated propanal (eq 2). There is a third possibility; i.e., the ion a could undergo a Wittig rearrangement (eq 3), a reaction that is known to be facile for deprotonated benzyl alkyl ethers and diallyl ethers.[10]



Scheme I



Scheme II



This paper addresses two questions: (i) what is the characteristic fragmentation of deprotonated allyl alkyl ethers and (ii) how does fragmentation behavior change for the homologous series of ions $CH_2{=}C\bar{C}H(CH_2)_nOEt$?

Experimental Section

Collisional activation mass spectra (MS/MS) were determined with a VG ZAB 2HF instrument. Full experimental details have been reported previously.[11] Specific details were as follows: A chemical ion-

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ization slit was used in the ion source, the ionizing energy was 70 eV, the ion source temperature was 150 °C, and the accelerating voltage was 7 kV. Samples were introduced through the septum inlet (maintained at 100 °C) (source pressure 5×10^{-7} Torr). Deprotonation was effected by using NH_2^- (from NH_3; source pressure 1×10^{-5} Torr). The estimated source pressure was 10^{-1} Torr. Helium was used in the second collision cell (measured pressure 2×10^{-7} Torr), giving a 10% reduction in the main beam. An electric sector scan was used. Consecutive collision-induced/charge-reversal[12] mass spectra (MS/MS/MS) were measured with a Kratos MS 50 TA instrument. Operating details have been reported previously.[13] Substrates were deprotonated by MeO^- (from MeONO)[14] in a Kratos Mark IV chemical ionization source: source temperature 100 °C, electron energy 280 eV, emission current 500 μA, and accelerating voltage 8 kV. The substrate pressure was 2×10^{-5} Torr, and the methyl nitrite pressure was 1×10^{-6} Torr: estimated source pressure 10^{-1} Torr. The indicated pressure of helium in each of the two collision cells was 2×10^{-6} Torr, giving a 30% reduction in the main beam.

All unlabeled ethers $CH_2{=}CH(CH_2)_nOR$ (n = 1–8, R = alkyl) were prepared by a reported procedure;[15] their purity was checked by GC, ^1H NMR, and positive-ion mass spectrometry. The following compounds are known: allyl methyl ether,[16] allyl ethyl ether,[17] allyl propyl ether,[17] 4-methoxybut-1-ene,[15] 4-ethoxybut-1-ene,[18] 5-methoxypent-1-ene,[19] 5-ethoxypent-1-ene,[20] and 6-methoxyhex-1-ene.[19] The following ethers have not been reported and were prepared by the standard reaction:[15] (i) 4-butoxybut-1-ene (bp 122–124 °C/760 mmHg, yield 41%, $M^{\cdot+}$ = 128.1193, $C_8H_{16}O$ requires 128.1201); (ii) 10-methoxydec-1-ene (bp 25–26 °C/0.012 mmHg, yield 23%, $M^{\cdot+}$ = 170.1671, $C_{11}H_{22}O$ requires 170.1664); (iii) 10-ethoxydec-1-ene (bp 28–30 °C/0.012 mmHg, yield 27%, $M^{\cdot+}$ = 184.1819, $C_{12}H_{24}O$ requires 184.1827).

The deuterium-labeled ethers were all made by the standard method using the starting materials ethyl-1,1-d_2 iodide,[21] ethyl-2,2,2,-d_3 iodide,[22] and prop-3-en-1-ol-1,1-d_2[23] (as appropriate). The incorporation of d_2 or d_3 was >98%.

The phenyl-substituted ethers were made by a reported procedure;[15] all compounds used in this study are known: 2-ethoxy-1-phenylethane,[24,25] 2-propoxy-1-phenylethane,[26] 3-methoxy-1-phenylpropane,[27] and 3-ethoxy-1-phenylpropane.[25] Cyclopropyl acetate[28] and $Me_3SiCH_2CH_2CHO$[29] were made by reported procedures.

Results and Discussion

The collisional activation mass spectra of the deprotonated ethers are listed in Table I or illustrated in Figure 2. The question as to whether the Wittig rearrangement occurs for the alkyl allyl ethers is answered by the very first spectrum shown in Table I—that of deprotonated methyl allyl ether. This spectrum exhibits losses of $H^\cdot$ and H_2; had the ion undergone the Wittig rearrangement (cf. eq 3), losses of CH_4 and C_2H_4 would have been noted.[10] There is no evidence for Wittig rearrangement of any of the allyl ethers shown in Table I. This is an unusual result since

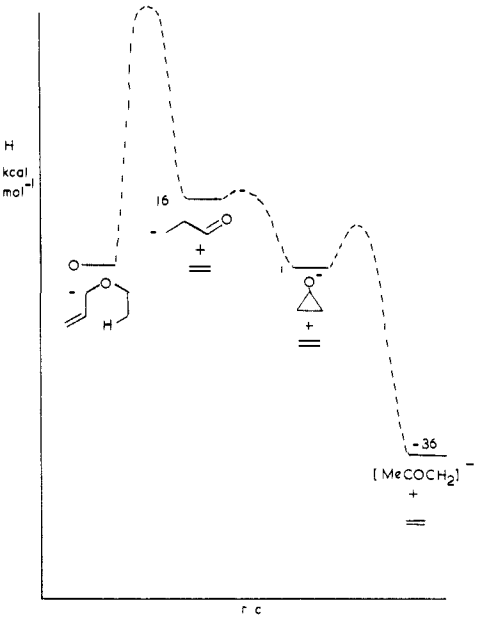
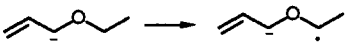


Figure 1. Mechanism suggested for the elimination of ethene from $CH_2{=}C\dot{C}HOEt$, using Benson's additivity rules,[33] DE(CH) and DE(OH) of 98 and 104 kcal mol^{-1}, respectively, and assuming electron affinities for (i) $CH_2{=}C\dot{C}HOEt$ of ≃4 kcal mol^{-1} [an average of $CH_2{=}CHCH_2^\cdot$ (8 kcal mol^{-1} [34]) and $MeOCH_2^\cdot$ (0 kcal mol^{-1} [8b]], (ii) $^\cdot CH_2CH_2CHO$ of ≃0, (iii) cyclo-$C_3H_5O^\cdot$ of ≃ 40 kcal mol^{-1} ($EtO^\cdot$ = 40 kcal mol^{-1} [32]), and (iv) $(MeCOCH_2)^\cdot$ of 40 kcal mol^{-1}.[34]

the corresponding deprotonated alkyl benzyl ethers fragment almost exclusively through the alkoxide ion formed by Wittig rearrangement.

(A) Alkyl Allyl Ethers. The characteristic fragmentations of ions $CH_2{=}C\dot{C}HOR$ (R ≥ Et) are best considered for the prototypical example of the ethyl derivative and its three deuterium-labeled derivatives (Table I). Deprotonation occurs at the allylic methylene group. There are two major decompositions: the loss of a hydrogen atom (eq 4) and elimination of ethene. The



(4)

loss of ethene occurs with transfer of a proton from the terminal methyl group and produces the base peak of the spectrum. The product peak is dish-shaped with a width at half-height of 116 ± 2 V. Wide dish-shaped peaks are also produced by losses of alkenes from other even-electron negative ions (e.g., ketone enolates[11,30] and alkyl amides[9b]) and are often associated with reactions with considerable reverse activation energies.[11] It has been suggested that the loss of ethene could produce either the allyloxy anion (eq 1) or deprotonated propanal (eq 2). Comparison of the CA and CR MS/MS/MS spectra of this ion (Table II) with the CA and CR MS/MS data for authentic $CH_2{=}CH{-}C\bar{H}_2O^-$ and $Me\bar{C}HCHO$ shows that it corresponds to neither of these species. The product ion of this reaction is identified as deprotonated acetone by the data given in Table II. An exactly similar result is given for allyl propyl ether (Table II). The only mechanism that appears to fit the available data is shown in eq 5, i.e., initial proton transfer to the methine position on the double bond, with formation of the ion b, which may rearrange to the cyclopropyloxy anion c, which in turn hydride ion transfers to form the deprotonated acetone ion.[31]

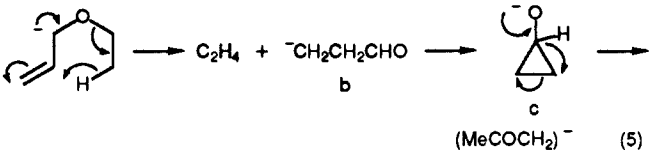


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Table I. Collisional Activation Mass Spectra of Deprotonated Ethers

	loss												formation						
parent ion	$H^•$	$D^•$	H_2	HD	C_2H_4	$C_2H_2D_2$	C_3H_6	C_4H_8	MeOH	EtOH	CD_3-CH_2OH	PrOH	$PhCH_2^-$	BuO^-	PrO^-	EtO^-	CD_3-CH_2O^-	Me-CD_2O^-	MeO^-
CH=CHĊHOMe	100		56																
CH_2=CHĊHOEt	45				100											5			
CH_2=CHĊDOEt	40				100											3			
CH_2=CHĊHOCD_2Me		31				100												2	
CH_2=CHĊHOCH_2CD_3	62					100											2		
CH_2=CHĊHOPr	30						100								8				
CH_2=CHĊDOPr	25						100								*a*				
CH_2=CHĊHCH_2OMe	5								8										100
CH_2=CHĊHCH_2OEt	8				100											28			
CH_2=CHĊHCH_2OCH_2CD_3	9					100											27		
CH_2=CHĊHCH_2OPr	16						100								86				
CH_2=CHĊHCH_2OBu	12							89						100					
CH_2=CHĊH$(CH_2)_2$OMe	19								21										100
CH_2=CHĊH$(CH_2)_2$OEt	21		5		100											73[b]			
CH_2=CHĊH$(CH_2)_3$OMe	28								15										100
CH_2=CHĊH$(CH_2)_7$OMe	35								100										10
CH_2=CHĊH$(CH_2)_7$OEt	100				45[c]					21						38[d]			
CH_2=CHĊH$(CH_2)_7$OCH_2CD_3	100					35[c]					17						29[f]		
PhĊHCH_2OEt	12		4		100								8			26			
PhĊHCH_2OPr	4		1				38					3	8		100[g]				57
PhĊH$(CH_2)_2$OMe	100								18										
PhĊH$(CH_2)_2$OEt	93				10					6			1			100[h]			
PhĊH$(CH_2)_2$OPr	87						4					2			100[g]				

[a] Not resolved, but <10%. [b] There is also an ($EtO^- - H_2$) ion (8%). [c] There is also an ion corresponding to $-(C_2H_4 + H_2)$ (ca. 15%, not resolved). [d] There is also an ($EtO^- - H_2$) ion (5%). [e] There is also an ion corresponding to $-(C_2H_2D_2 + H_2)$ (ca. 10%, not resolved). [f] There is also an ($CD_3CH_2O^-$ – HD) ion (4%). [g] There is also an ($PrO^- - H_2$) ion (16%). [h] There is also an ($EtO^- - H_2$) ion (6%).

Table II. Collisional Activation and Charge-Reversal MS/MS/MS of $C_3H_5O^-$ Product Ions together with MS/MS Data of $C_3H_5O^-$ Anions of Known Structure

		m/z (abundance)																				
ion (origin)	spectrum type	56	55	54	53	43	42	41	40	39	38	37	31	30	29	28	27	26	25	15	14	13	12
$C_3H_5O^-$ (allyl ethyl ether)	CA MS/MS/MS	100						42		3													
	CR MS/MS/MS	3	12	1	4	61	100	25	5	57	11	5			44	12	52	19	4	9	8	1	0.5
$C_3H_5O^-$ (allyl propyl ether)	CA MS/MS/MS	100						37		3													
	CR MS/MS/MS	3	14	1	3	63	100	24	4	60	13	4			47	14	50	21	3	10	8	1	0.5
CH_2=CHCH_2O^- (allyl alcohol)	CA MS/MS	77	100					21		5					24		60	3	3				
	CR MS/MS	3	68	1	4	6	20	27	11	77	11	4	6	8	71	27	100	40	4	3	4	0.5	
MeĊHCHO (propanal)	CA MS/MS	98	100				7	11		2					1		4		2				
	CR MS/MS	17	43	3	4		3	9	4	46	6	3	3		100	32	63	31	3	3	4	1	
$MeCOCH_2^-$ (acetone)	CA MS/MS	100						41		3													
	CR MS/MS	2	10	1	4	68	100	22	8	57	11	5			43	11	49	20	3	10	8	1	0.5
"$\overline{CH_2CH_2CHO}^-$" (cyclopropyl acetate)	CA MS/MS	100						35		2													
	CR MS/MS	2	12	1	3	60	100	22	8	61	12	4			51	15	50	22	3	9	9	1	0.5
"$^-CH_2CH_2CHO$" ($Me_3Si(CH_2)_2CHO$)	CA MS/MS	100						40		3													
	CR MS/MS	2	10	1	4	62	100	23	12	65	11	3			56	17	50	21	4	11	9	1	0.5

Table III. Collisional Activation and Charge-Reversal MS/MS/MS of $C_4H_7O^-$ Product Ions together with MS/MS Data of $C_4H_7O^-$ Ions of Known Structure

ion (origin)	spectrum type	m/z (abundance)																
		70	69	68	55	53	45	43	42	41	39	31	30	29	28	27	26	15	14
$C_4H_7O^-$ (butenyl propyl ether)	CA MS/MS/MS[a]		100		26			47											
	CR MS/MS/MS[a]	5	11		100	27	9	97	40	32	53			38	26	85	32	9	2
$CH_2{=}CH(CH_2)_2O^-$ (but-3-en-1-ol)	CA MS/MS		100		27			61											
	CR MS/MS	3	8		100	22	10	94	38	27	45			35	24	83	30	8	2
$MeCH{=}CHCH_2O^-$ (crotyl alcohol)	CA MS/MS	11	58		2	1		4		100									
	CR MS/MS	3	21	1	24	17		17	21	65	100	3	4	38	11	40	12	4	1

[a] Weak spectra; time average of 100 scans.

Table IV. Collisional Activation and Charge-Reversal MS/MS/MS of $C_5H_9O^-$ Product Ions together with MS/MS Data of $CH_2{=}CH(CH_2)_3O^-$

ion (origin)	spectrum type	m/z (abundance)													
		83	68	67	55	54	53	51	41	39	29	28	27	26	15
$C_5H_9O^-$ (pentenyl ethyl ether)	CA MS/MS/MS[a]	18		*b*	100										
	CR MS/MS/MS[a]	5	10	10	97	36	47	16	54	100	59	19	61	14	*b*
$CH_2{=}CH(CH_2)_3O^-$ (pent-4-en-1-ol)	CA MS/MS	10		2	100										
	CR MS/MS	5	10	11	93	36	44	18	66	100	62	22	52	12	3

[a] Weak spectrum; time average of 100 scans. [b] Not observed because of base-line noise.

In order to test the hypothesis outlined in eq 5, we have attempted to prepare the ion b by the standard $S_N2(Si)$ reaction[32] shown in eq 6. When Nu = MeO, a pronounced peak is formed

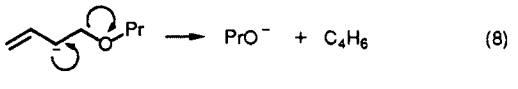
$$Nu^- + Me_3SiCH_2CH_2CHO \longrightarrow \underset{b}{^-CH_2CH_2CHO} + Me_3SiNu \quad (6)$$

$$Nu^- + MeCO{-}O{-}\triangleleft \longrightarrow (MeCOCH_2)^- + MeCONu \quad (7)$$

at m/z 57; its CA and CR mass spectra are identical with those of deprotonated acetone. Thus the ion b is a transient species, transforming to the more stable $(MeCOCH_2)^-$ ion. In addition, when cyclopropyl acetate is treated with MeO^- in the source of the MS 50 TA instrument, the CA and CR mass spectra of the product ion $C_3H_5O^-$ also identify it as $(MeCOCH_2)^-$, not cyclo-$C_3H_5O^-$ (see Table II). Thus the mechanism shown in eq 5 fits the available data, but it is not clear why it occurs in preference to the reactions shown in eqs 1 and 2.

A rough estimation of the thermochemistry of each process can be determined by using Benson's additivity rules[33] together with bond dissociation energies and known (or estimated) electron affinities. In the case of enolate anions, the more stable O^- structure is used in the calculation. We calculate that the processes shown in eqs 1, 2, and 5 are exothermic by 4, 32, and 36 kcal mol^{-1}, respectively. Thus the observed process (see Figure 1) is favored thermodynamically. On the other hand, the initial proton transfer in this case must be less favored than either proton transfer shown in eqs 1 and 2.

(B) Decompositions of Ions $CH_2{=}C\bar{C}H(CH_2)_nOR$ (n = 1-7). The CA MS/MS plots are shown in Table I with a representative spectrum shown in Figure 2. The spectrum shown in Figure 2 exhibits the characteristic dish-shaped peak at m/z 71 (a process that is predominantly collision-induced; see legend to Figure 2) and the simple alkoxide displacement shown in eq 8.



(8)

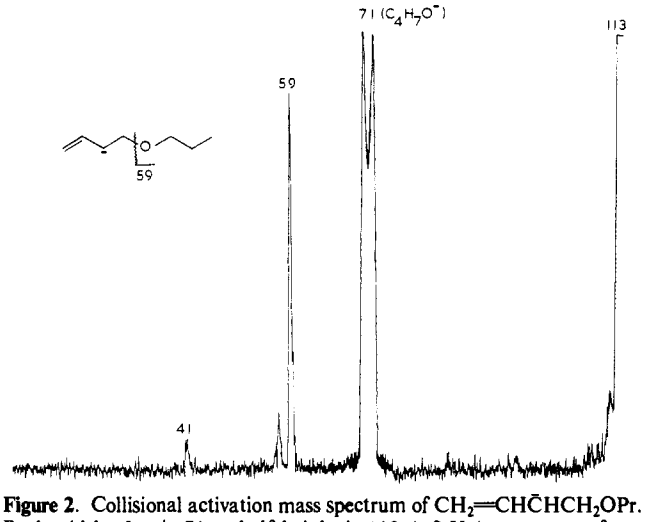


Figure 2. Collisional activation mass spectrum of $CH_2{=}C\bar{C}HCH_2OPr$. Peak width of m/z 71 at half-height is 118 ± 2 V (an average of ten individual scans). When a potential of +1000 V is applied to the collision cell, 15% of decompositions forming m/z 71 occur outside the collision cell.

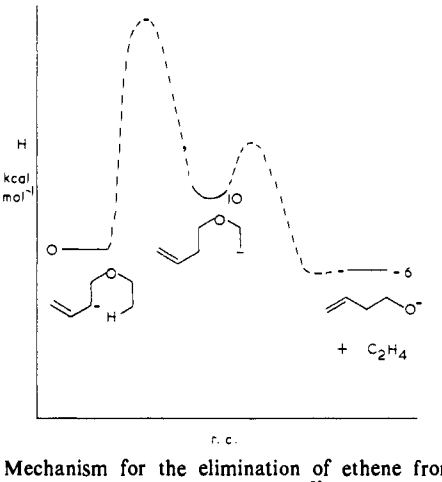


Figure 3. Mechanism for the elimination of ethene from $CH_2{=}C\bar{C}HCH_2OEt$, using Benson's additivity rules,[33] DE(CH) and DE(OH) of 98 and 104 kcal mol^{-1}, respectively, and assuming electron affinities for (i) $CH_2{=}C\bar{C}H_2CH_2OEt$ of 8 kcal mol^{-1} ($CH_2{=}CHCH_2^\cdot$ = 8 kcal mol^{-1}),[34] (ii) $CH_2{=}CH(CH_2)_2O\bar{C}H_2CH_2^\cdot$ of ≃0, and (iii) $CH_2{=}CH(CH_2)_2O^-$ of ≃ 40 kcal mol^{-1} ($EtO^\cdot$ = 40 kcal mol^{-1}).[34]

The next question to be answered concerns the mechanism of alkene elimination from these ions. The data collected in Tables III and IV shows that the losses of ethene from $CH_2{=}C\bar{C}H$-

(31) Similar interconversions have been considered for cognate systems (Noest, A. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1980**, *102*, 6427; see also: Peerboom, R.; Ingemann, S.; Nibbering, N. M. M. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 74). Consider $^-CH_2Me_2CCHO$: in this case it was concluded that homoconjugation did not lead to appreciable amounts of ring-closed ions and that the product ion was mainly $^-CH_2Me_2CCHO$. The same studies demonstrate that substituted cyclopropoxy anions may undergo isomerization following ring cleavage.

(32) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 6443. Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

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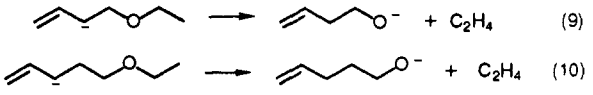
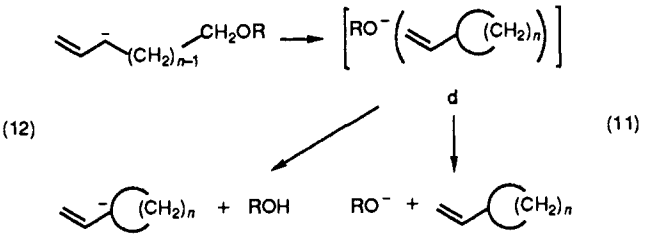
$(CH_2)_nOEt$ (n = 1, 2) occur by β-proton transfer to the initial carbanion center followed by alkene elimination to produce the expected alkoxide ion (see eqs 9 and 10). A suggested mechanistic profile for the former reaction is shown in Figure 3; in this case the proton transfer occurs through a six-center state.



Surprisingly, the elimination reaction even occurs when n = 7 (Table I), but as n increases, the competing reactions shown in eqs 11 and 12 increase with respect to the alkene elimination. The formulation of these product ions is rationalized as proceeding through the ion complex d.



(C) **Decompositions of Ions $PhCH(CH_2)_nOR$.** A similar but more pronounced effect is noted in the spectra of the phenyl derivatives listed in Table I. Except for $PhCHCH_2OEt$ (where loss of C_2H_4 gives the base peak), elimination of the alkene is less pronounced than formation of RO^-. In this series, the abundance of the peak produced by elimination of the alkene decreases as both n and R increase.

Conclusion

(i) The characteristic decomposition of the species $CH_2{=}CHCH(CH_2)_nOEt$ (n = 1, 2) is the E1cB elimination of ethene following β-proton transfer to the initial carbanion site. The reaction is most pronounced when the β-proton transfer to the initial carbanion site occurs through a six-center transition state. The elimination process occurs even when n = 7. The latter observation emphasizes the proclivity of proton-transfer reactions in such systems even when the carbanion center is remote from the proton-donor site. (ii) When n = 0, the expected elimination reaction does not occur, i.e., where β-proton transfer to the initial carbanion center requires a five-center state. Instead, proton transfer occurs to the adjacent methine position with the ultimate formation of $(MeCOCH_2)^-$ as the sole ionic species.

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L-Edge Spectroscopy of Molybdenum Compounds and Enzymes[ƒ]

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Abstract: Spectra at the molybdenum L_2 and L_3 edges have been recorded by use of synchrotron radiation and analyzed in terms of ligand field theory. Four distinct p → d transitions were observed in the derivative spectra of molybdenum oxychloride complexes. Comparison with optical data for the same compounds, as well as for Tc analogues, showed that $L_{2,3}$-edge spectra qualitatively reflect the unfilled Mo d-level splittings. A semiempirical correlation scheme, using Racah parameters to correct for exchange and Coulomb interactions, predicted optical splittings with an accuracy of better than 5%. This capability was used to reject certain interpretations of the MoO_4^{2-}, $MoOCl_4(H_2O)^-$, and $MoOCl_5^-$ spectra. Single-crystal spectra for $[N(Et)_4][MoOCl_4(H_2O)]$ helped confirm the assignments. Chemical effects on Mo L-edge spectra were surveyed for LMoOXY compounds, where L represents hydrotris(3,5-dimethyl-1-pyrazolyl)borate and X and Y are various ligands. Spectral sensitivity to oxidation state, terminal oxo vs terminal sulfido ligands, and different halide ions are also compared. Preliminary spectral analysis of several molybdenum enzymes is presented. L_3-edge splittings of 1.72 and 1.40 eV were observed for nitrogenase and active xanthine oxidase, respectively. Oxidized sulfite oxidase gave L_3-edge splittings of 1.05, 2.14, and 3.05 eV. L-edge spectroscopy is a useful technique for studying molybdenum in small molecules, enzymes, and catalysts, especially if such materials are available in oriented forms.

Molybdenum K-edge X-ray absorption has been used for the study of molybdenum enzymes,[1] aqueous solutions,[2] amorphous materials,[3,4] and catalysts.[5] Although the experimental conditions at 20 keV are ideal for EXAFS, utilization of the K-edge XANES is hindered by the 6-eV natural line width for the K hole.[6] Furthermore, angular momentum selection rules restrict the types of transitions that can be observed at the K edge to final states

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[ƒ] Bicine, *N,N*-bis(2-hydroxyethyl)glycine; Tris, 2-amino-2-(hydroxymethyl)-1,3-propanediol; Bis-Tris, 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol; L, hydrotris(3,5-dimethyl-1-pyrazolyl)borate, pip, *N*-hydroxypiperidine; PyH, pyridinium ion, EXAFS, extended X-ray absorption fine structure; XANES, X-ray absorption near-edge structures; fwhm, full width at half-maximum.

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