

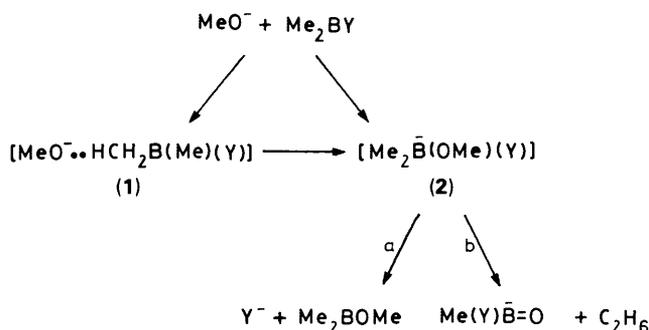
Are Tetrahedral Intermediates Formed by Addition of Nucleophiles to Organoboranes in the Gas Phase?

Graeme J. Currie, John H. Bowie, Kevin M. Downard, and John C. Sheldon
 Departments of Chemistry, University of Adelaide, South Australia, Australia, 5001

Nucleophilic addition of CD_3O^- to Me_2BOMe gives the same addition product as the corresponding reaction between Me_2BOCD_3 and MeO^- , as evidenced by the identical collisional activation mass spectra of the products. This is interpreted in terms of exclusive formation of a boron product ion of tetrahedral geometry. The decompositions of the product involve loss of MeOH and CD_3OH and the formation of MeO^- and CD_3O^- . The major decompositions of $(\text{CD}_3)_3\text{B} + ^-\text{OCH}_2\text{CH}_2\text{XMe}$ ($\text{X} = \text{O}, \text{S}, \text{or NMe}_2$) are similar to those outlined above and may be explained by initial formation of $(\text{CD}_3)_3\text{B}^-\text{OCH}_2\text{CH}_2\text{XMe}$. However, there are some unusual fragmentations (*e.g.* loss of CH_3D) which may occur through the alternative structure $(\text{CD}_3)_3\text{B}^+\text{X}(\text{Me})\text{CH}_2\text{CH}_2\text{O}^-$. It is suggested that other ambident species may also react with Me_3B to form several tetrahedral species, *e.g.* deprotonated

methyl acetate could yield $\text{Me}_3\text{B}^-\text{CH}_2\text{CO}_2\text{Me}$, $\text{Me}_3\text{BOC}(\text{OMe})=\text{CH}_2$, and $\text{Me}_3\text{B}^-\text{O}^+(\text{Me})\text{C}(\text{O})\text{CH}_3$. The formation of the third structure is supported by the pronounced loss of ketene from this system.

A joint *ab initio*/ion cyclotron resonance (i.c.r.) study of the nucleophilic addition of methoxide ion to organoboranes suggested the mechanistic pathways shown in Scheme 1 ($\text{Y} =$



Scheme 1.

OR).¹ Initial approach of the nucleophile can either (i) hydrogen bond to form an ion complex (1) which is readily converted into the tetrahedral species (2) over a small barrier, or (ii) attack the central boron directly to form (2). Intermediate (2) generally lies some 200 kJ mol^{-1} lower in energy than (1), and the direct pathway to (2) is the more probable approach. Intermediate (2) decomposes principally to effect nucleophilic displacement [pathway (a)], but more complex reactions may also occur [*e.g.* pathway (b)].

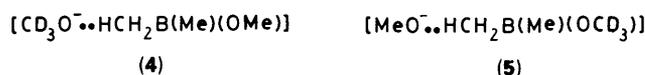
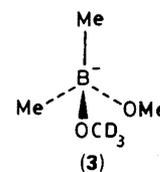
The i.c.r. spectra of $\text{MeO}^-/\text{Me}_2\text{BY}$ systems contain pronounced peaks corresponding to non-decomposing adducts $[\text{MeO}^- + \text{Me}_2\text{BY}]$; such species must be stabilized by collisional deactivation (or a radiative process) in the i.c.r. cell. It would be of interest to determine the structures of such adducts: for example, do they correspond to the tetrahedral structures (2)? Information can sometimes be obtained (from product ion studies) about the nature of decomposing intermediates in i.c.r. studies, but usually not about non-decomposing ions. This problem can be overcome if non-decomposing ions can be formed in a conventional mass spectrometer, and forced to

fragment by subjecting them to collisional activation. The present study reports the formation of such adducts in the chemical ionization source of a VG ZAB 2HF mass spectrometer, and addresses three interrelated questions: (i) what are the structures of stable adducts $\text{RO}^- + \text{Me}_2\text{BY}$? (ii) how do these species behave when collisionally activated? and (iii) what species are formed by reaction of an ambident nucleophile with Me_2BY ?

Results and Discussion

Collisional activation (c.a.) mass spectra were determined with a VG ZAB 2HF mass spectrometer using helium as the collision gas. Full details are described in the Experimental.

The Structure of the Non-decomposing Adducts.—*ab initio* calculations suggest that the two stable species, (1) and (2) (Scheme 1) may be formed when MeO^- is allowed to react with Me_2BY . These two ions should fragment differently upon collisional activation. Let us consider a simple experiment. Reaction of Me_2BOMe with CD_3O^- and reaction of Me_2BOCD_3 with MeO^- should give the same tetrahedral product (3), a species with a C_2 axis of symmetry. Thus if the

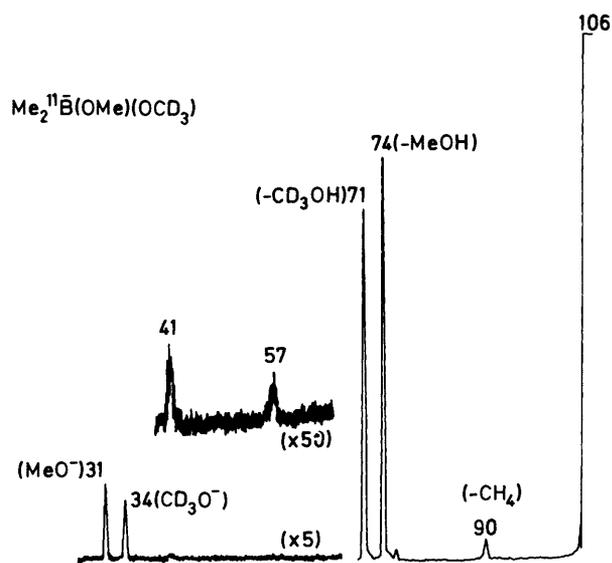


stable adduct is tetrahedral, the collisional activation spectra of the $(\text{Me}_2\text{BOMe} + \text{CD}_3\text{O}^-)$ and $(\text{Me}_2\text{BOCD}_3 + \text{MeO}^-)$ ions should be identical. In contrast, should the H-bonded species

Table 1. C.a. mass spectra of organoborane-alkoxide adducts [loss (relative abundance – % strongest peak)].

Parent ion	H ⁺	H ₂	CH ₄	C ₂ H ₆	CH ₂ O	MeOH	MeCHO	CD ₃ CDO	EtOH
Me ₂ ¹¹ BOMe + MeO ⁻	4		3		4	100			
Me ₂ ¹¹ BOEt + EtO ⁻	4		4				7		100
Me ₂ ¹¹ BOEt + C ₂ D ₅ O ⁻	10		18				8	2	100
Me ₂ ¹¹ BOC ₂ D ₅ + EtO ⁻	10		16	1			7	2	100
Et ₂ ¹¹ BOEt + EtO ⁻		4					9		100
(MeO) ₃ ¹¹ B + MeO ⁻					21	25			

Parent ion	C ₂ D ₅ OH	Me ₂ O	(CH ₄ + Me ₂ O)	Et ₂ O	Me ₂ BOMe	Me ₂ BOEt	Me ₂ BOC ₂ D ₅	Et ₂ BOEt	(MeO) ₃ B
Me ₂ ¹¹ BOMe + MeO ⁻		0.6	0.8		22				
Me ₂ ¹¹ BOEt + EtO ⁻						8			
Me ₂ ¹¹ BOEt + C ₂ D ₅ O ⁻	83					13	16		
Me ₂ ¹¹ BOC ₂ D ₅ + EtO ⁻	83					12	15		
Et ₂ ¹¹ BOEt + EtO ⁻				1				14	
(MeO) ₃ ¹¹ B + MeO ⁻		20							100

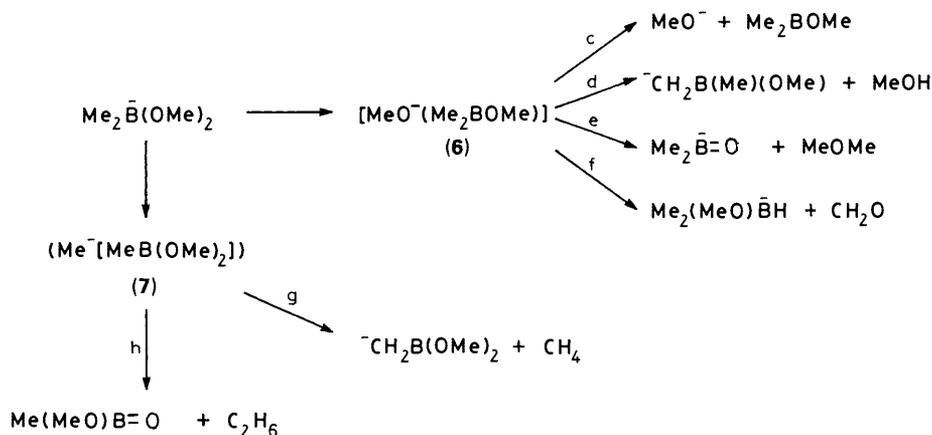
**Figure 1.** Collisional activation mass spectrum of Me₂B(OMe)(OCD₃), see the Experimental for details.

spectra of the (Me₂BOMe + CD₃O⁻) and (Me₂BOCD₃ + MeO⁻) adducts are identical and are illustrated in Figure 1. In a similar way, the c.a. mass spectra of (Me₂BOEt + C₂D₅O⁻) and (Me₂BOC₂D₅ + EtO⁻) ions are, within experimental error, identical (see Table 1). These results are consistent with the stable adducts having tetrahedral geometry.*

The Fragmentations of Four-co-ordinate Boron Negative Ions.

—*Negative ions formed with simple alkoxide ions.* The c.a. mass-spectra of these species are recorded in Table 1 and illustrated in Figure 1. Fragmentation behaviour may be illustrated by reference to Me₂B(OMe)₂; a summary is given in Scheme 2.

Most of the fragmentations shown in Scheme 2 are standard reactions of the type observed for the analogous silicon^{3,4} and phosphorus ions.⁵ Fragmentations of such species are considered to proceed *via* the intermediacy of ion complexes^{4,6} although in some cases radical-radical anion complexes may be involved.⁷ We rationalize all fragmentations in terms of the intermediacy of ion complexes (6) and (7) (Scheme 2). The major fragmentations are the formation of MeO⁻ [pathway (c)], and the elimination of MeOH [pathway (d)], and CH₄ [pathway (g)]. Secondary deuterium isotope effects H/D of 1.23 and 1.15 are observed for MeO⁻ formation and MeOH loss (see Figure 1). Minor reactions are the S_Ni processes [pathways (e) and (h)].

**Scheme 2.**

be formed, then Me₂BOMe + CD₃O⁻ will give (4) and Me₂BOCD₃ + MeO⁻, (5). Ions (4) and (5) will fragment differently; (4) will competitively form CD₃O⁻ and eliminate CD₃OH, while (5) will give MeO⁻ and eliminate MeOH. If Me₂BOMe/CD₃O⁻ gives a mixture of (3) and (4), and Me₂BOCD₃/MeO⁻ a mixture of (3) and (5), then the composite spectra will again be different. The collisional activation

* The c.a. spectra of the two adducts (Me₃SiOMe + CD₃O⁻) and (Me₃SiOCD₃ + MeO⁻) are different.² Whether this is due to non-equilibration of apical and equatorial substituents in a trigonal bipyramidal intermediate³ or the formation of ion complexes analogous to (4) and (5) is not known. The important observation is that the two spectra are different.

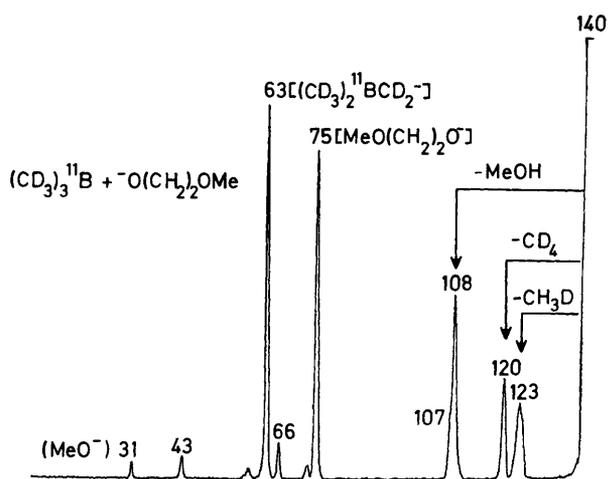
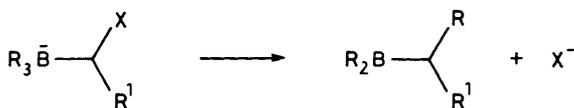


Figure 2. Collisional activation mass spectrum of the addition product(s) formed between $(\text{CD}_3)_3\text{B}$ and $^-\text{OCH}_2\text{CH}_2\text{OMe}$.

and (h)] and the hydride-ion transfer [pathway (f)]. The hydride-ion transfer is notable since this type of reaction has not been observed before in gas-phase boron chemistry. The methoxide ion is known to be an ambident species in the gas phase—it may transfer hydride ion to formaldehyde^{8,9} and other neutrals such as sulphur dioxide.⁹ In the present case the product is a borohydride anion [pathway (f)]. The reaction becomes more pronounced as the number of methoxy groups around B increases; in the case of $[(\text{MeO})_4\text{B}]^-$, loss of CH_2O gives a peak of 21% abundance (Table 1).

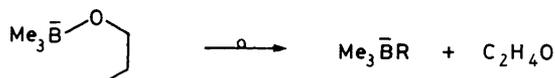


Scheme 3.

Negative ions formed from bifunctional alkoxide ions. The occurrence of the hydride-transfer reactions described above, together with the reports of rearrangement products arising from condensed-phase reactions of organoboranes^{10,11} (e.g. Scheme 3, X=F, HO, MeO, MeS, and Me_2N), has led us to consider the c.a. spectra of adducts formed between Me_3B and alkoxide ions $^-\text{O}(\text{CH}_2)_2\text{R}$ (R = F, HO, MeO, MeS, and Me_2N). The primary purpose of this phase of the investigation was to ascertain whether migration of R to the boron centre occurs for ions $\text{Me}_3\text{BOCH}_2\text{CH}_2\text{R}$.

The collisional activation spectra are recorded in Table 2, and a particular example is illustrated in Figure 2. The spectra are complex, and recourse to extensive deuterium labelling was necessary to determine the origin of the fragments lost. Full details are provided in Table 2. All of these ions decompose by some of the major pathways outlined in Scheme 2, viz. (i) formation of $\text{R}(\text{CH}_2)_2\text{O}^-$, cf. pathway (c) (m/z , 75, Figure 2), (ii) elimination of $\text{R}(\text{CH}_2)_2\text{OH}$, cf. pathway (d) (m/z , 63, Figure 2), (iii) hydride transfer by specific loss of RCH_2CHO , cf. pathway (f) (m/z , 66, Figure 2), and (iv) loss of methane, cf. pathway (g) (m/z , 120, Figure 2).

In addition to the standard reactions described above, all spectra show apparent rearrangement peaks including some that have no analogy with any reported negative ion cleavage. The first involves migration of R to boron (Scheme 4), but only



Scheme 4.

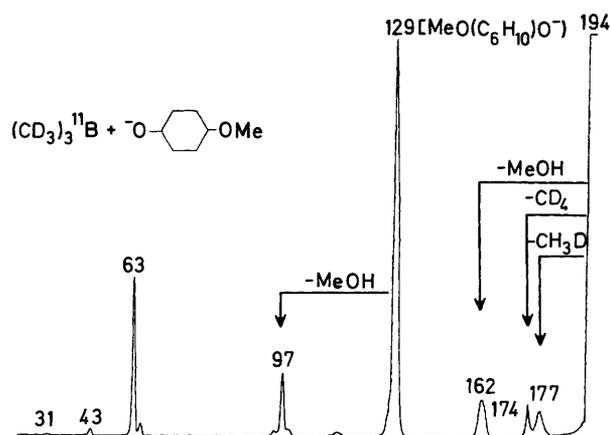
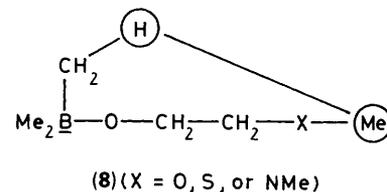
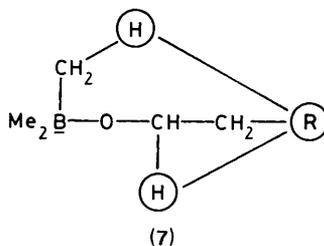


Figure 3. Collisional activation mass spectrum of the addition product(s) formed between $(\text{CD}_3)_3\text{B}$ and $^-\text{O}(\text{C}_6\text{H}_{10})\text{OMe}$.

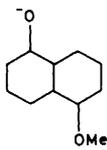
occurs when R = F or OH. The other rearrangements are (i) the loss of RH from all systems studied, and (ii) a second loss of methane, occurring when R = MeO, MeS, or Me_2N . Labelling studies (Figure 2, Table 2) show that there are two losses of RH. These are represented in pictorial form in formula (7); the major loss always involves hydrogen loss from the methylene group adjacent to O (e.g. see Figure 2, m/z 107 and 108). In contrast, the loss of methane is always specific involving those atoms shown in formula (8) (e.g. see Figure 2 m/z 123).



The data in Table 2 indicate that these fragmentations are little affected by extending the side chain, i.e. for $^-\text{O}(\text{CH}_2)_n\text{R}$ where $n = 2-5$. They are likewise unaffected by building rigidity into the side chain; cf. Figures 2 and 3 (Figure 3 shows the case of a cyclohexane derivative) and Table 2 (for the analogous case of a decalin derivative).

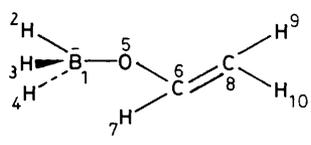
We have reported a set of 'rules' for the fragmentation of simple negative ion systems, including enolates, C^- , N^- , and O^- systems.¹² Elimination of neutral fragments from such ions is generally initiated through the charged centre and proceeds through ion complexes. A similar rationale^{4,6} is used for the fragmentations described in Scheme 2, except in this case the negative charge is a consequence of bonding in the boron system rather than being associated with a non-bonding pair of electrons. It has also been suggested that some reactions occur remote from (and uninfluenced by) the negative charge.¹³ Thus there appear to be two possibilities for these unusual reactions; (i) they are remote fragmentations of unknown mechanism, or (ii) since the reactions are uninfluenced by the length or nature

Table 2. C.a. mass spectra of Me₃¹¹B [and (CD₃)₃¹¹B] plus functionalized alkoxide ions.

Adduct	<i>m/z</i>	<i>m/z</i> (loss) abundance ^a
Me ₃ B + F(CH ₂) ₂ O ⁻	119	103 (CH ₄) 24, 99 (HF) 3, 75 (C ₂ H ₄ O) 10, 63 (Me ₃ B) 98, 57 (FCH ₂ CHO) 24, 55 [F(CH ₂) ₂ OH] 100, 19 (C ₅ H ₁₃ BO) 6
Me ₃ B + FCH ₂ CD ₂ O ⁻	121	105 (CH ₄) 38, 101 (HF) 3, 100 (DF) 1, 75 (C ₂ H ₂ D ₂ O) 4, 65 (Me ₃ B) 82, 58 (FCH ₂ CDO) 19, 55 (FCH ₂ CD ₂ OH) 100, 19 (C ₅ H ₁₁ D ₂ BO) 5
(CD ₃) ₃ B + F(CH ₂) ₂ O ⁻	128	109 (CD ₃ H, HF) 6, 108 (CD ₄ , DF) 13, 84 (C ₂ H ₄ O) 8, 66 (FCH ₂ CHO) 24, 63 [(CD ₃) ₃ B, F(CH ₂) ₂ OD] 100, 19 (C ₅ H ₄ D ₉ BO) 6
Me ₃ B + HO(CH ₂) ₂ O ⁻	117	116 (H ⁺) 4, 101 (CH ₄) 50, 99 (H ₂ O) 8, 86 (CH ₂ O) 6, 73 (C ₂ H ₄ O) 9, 61 (Me ₃ B) 100, 59 (Me ₃ B + H ₂) 9, 57 (HOCH ₂ CHO) 13, 55 [HO(CH ₂) ₂ OH] 12, 43 (Me ₃ B + H ₂ O), 15 (C ₄ H ₁₁ BO ₂) 0.5
Me ₃ B + DO(CH ₂) ₂ O ⁻	118	117 (H ⁺) 3, 102 (CH ₄) 16, 101 (CH ₃ D) 28, 99 (HOD) 6, 87 (CH ₂ O) 2, 86 (CHDO) 3, 74 (C ₂ H ₄ O) 7, 62 (Me ₃ B) 100, 59 (Me ₃ B + HD) 12, 57 (DOCH ₂ CHO) 12, 55 [DO(CH ₂) ₂ OH] 12, 43 (Me ₃ B + HOD) 2, 15 (C ₄ H ₁₀ DBO ₂) 0.3
Me ₃ B + MeO(CH ₂) ₂ O ⁻	131	115 (CH ₄) 52, 99 (MeOH) 38, 75 (Me ₃ B) 58, 57 (MeOCH ₂ CHO) 9, 55 [MeO(CH ₂) ₂ OH] 100, 43 (Me ₃ B + MeOH) 2, 31 (C ₅ H ₁₃ BO) 1
Me ₃ B + CD ₃ O(CH ₂) ₂ O ⁻	134	118 (CH ₄) 26, 114 (CD ₃ H) 9, 99 (CD ₃ OH) 18, 78 (Me ₃ B) 42, 57 (CD ₃ OCH ₂ CHO) 9, 55 [CD ₃ O(CH ₂) ₂ OH] 100, 43 (Me ₃ B + CD ₃ OH) 2, 34 (C ₅ H ₁₃ BO) 2
Me ₃ B + MeOCH ₂ CD ₂ O ⁻	133	117 (CH ₄) 32, 101 (MeOH) 6, 102 (MeOD) 14, 77 (Me ₃ B) 45, 58 (MeOCH ₂ CDO) 6, 55 (MeOCH ₂ CD ₂ OH) 100, 44 (Me ₃ B + MeOD) 2, 31 (C ₅ H ₁₁ D ₂ BO) 3
(CD ₃) ₃ B + CD ₃ O(CH ₂) ₂ O ⁻	143	124 (CD ₃ H) 15, 123 (CD ₄) 38, 108 (CD ₃ OH) 29, 107 (CD ₃ OH) 29, 107 (CD ₃ OD) 16, 78 [(CD ₃) ₃ B] 82, 66 (CD ₃ OCH ₂ CHO) 9, 63 [CD ₃ O(CH ₂) ₂ OH] 100, 43 [(CD ₃) ₃ B + CD ₃ OH] 3, 34 (C ₅ H ₄ D ₉ BO) 3
Me ₃ B + MeO(CH ₂) ₃ O ⁻	145	129 (CH ₄) 48, 103 (MeOH) 21, 89 (Me ₃ B) 76, 87 (Me ₃ B + H ₂) 16, 58 [MeO(CH ₂) ₂ CDO] 8, 55 [MeO(CH ₂) ₃ OH] 100, 31 (C ₆ H ₁₅ BO) 5
[(CD ₃) ₃ B] + MeO(CH ₂) ₃ O ⁻	154	138 (CH ₄) 18, 137 (CH ₃ D) 9, 134 (CD ₄) 30, 109 (MeOH) 3, 108 (MeOD) 4, 89 [(CD ₃) ₃ B] 100, 87 [(CD ₃) ₃ B + H ₂] 12, 66 [MeO(CH ₂) ₂ CHO] 9, 63 [MeO(CH ₂) ₃ OH] 78, 31 (C ₆ H ₆ D ₉ BO) 6
Me ₃ B + MeO(CH ₂) ₂ CD ₂ O ⁻	147	131 (CH ₄) 47, 115 (MeOH) 25, 91 (Me ₃ B) 78, 88 (Me ₃ B + -HD) 17, 58 [MeO(CH ₂) ₂ CDO] 6, 55 [MeO(CH ₂) ₂ CD ₂ OH] 100, 31 (C ₆ H ₁₃ D ₂ BO) 6
Me ₃ B + MeO(CH ₂) ₄ O ⁻	159	143 (CH ₄) 79, 127 (MeOH) 16, 103 (Me ₃ B) 28, 101 (Me ₃ B + H ₂) 6, 57 [MeO(CH ₂) ₃ CHO] 12, 55 [MeO(CH ₂) ₄ OH] 100, 31 (C ₇ H ₁₇ BO) 8
Me ₃ B + MeO(CH ₂) ₅ O ⁻	173	157 (CH ₄) 47, 141 (MeOH) 13, 117 (Me ₃ B) 16, 115 (Me ₃ B + H ₂) 8, 57 [MeO(CH ₂) ₄ CHO] 13, 55 [MeO(CH ₂) ₅ OH] 100, 31 (C ₈ H ₁₉ BO) 7
Me ₃ B + Me ₂ N(CH ₂) ₂ O ⁻	144	128 (CH ₄) 66, 99 (Me ₂ NH) 22, 88 (Me ₃ B) 72, 86 (Me ₃ B + H ₂) 13, 57 (Me ₂ NCH ₂ CHO) 8, 55 [Me ₂ N(CH ₂) ₂ OH] 100, 43 (Me ₃ B + Me ₂ NH) 4
Me ₃ B + Me ₂ NCH ₂ CD ₂ O ⁻	146	130 (CH ₄) 88, 101 (Me ₂ NH) 6, 100 (Me ₂ ND) 10, 90 (Me ₃ B) 73, 87 (Me ₃ B + HD) 9, 58 (Me ₂ NCH ₂ CDO) 6, 55 (Me ₂ NCH ₂ CD ₂ OH) 100, 44 (Me ₃ B + Me ₂ ND) 3
Me ₃ B + (CD ₃) ₂ N(CH ₂) ₂ O ⁻	150	134 (CH ₄) 78, 131 (CD ₃ H) 38, 99 [(CD ₃) ₂ NH] 29, 94 (Me ₃ B) 84, 92 (Me ₃ B + H ₂) 16, 57 [(CD ₃) ₂ NCH ₂ CHO] 8, 55 [(CD ₃) ₂ N(CH ₂) ₂ OH] 100, 43 [Me ₃ B + (CD ₃) ₂ NH] 5
(CD ₃) ₃ B + Me ₂ N(CH ₂) ₂ O ⁻	153	137 (CH ₄) 32, 134 (CD ₃ H) 16, 133 (CD ₄) 25, 108 (Me ₂ NH) 24, 107 (Me ₂ ND) unresolved, 88 [(CD ₃) ₃ B] 100, 86 [(CD ₃) ₃ B + H ₂] 16, 66 (Me ₂ NCH ₂ CHO) 8, 63 [Me ₂ N(CH ₂) ₂ OH] 96, 43 [(CD ₃) ₃ B + Me ₂ NH]
Me ₃ B + Me ₂ N(CH ₂) ₃ O ⁻	158	142 (CH ₄) 80, 113 (Me ₂ NH) 24, 102 (Me ₃ B) 100, 100 (Me ₃ B + H ₂) 21, 57 [Me ₂ N(CH ₂) ₂ CHO] 6, 55 [Me ₂ N(CH ₂) ₃ OH] 100
Me ₃ B + MeS(CH ₂) ₂ O ⁻	147	132 (Me ⁺) 10, 131 (CH ₄) 18, 99 (MeSH) 39, 91 (Me ₃ B) 100, 75 (C ₄ H ₁₃ B) 10, 57 (MeSCH ₂ CHO, MeSCH ₂ CH ₂ Me) 18, 55 (MeSCH ₂ CH ₂ OH) 46, 47 (C ₅ H ₁₃ BO) 20, 43 (Me ₃ B + MeSH) 6
(CD ₃) ₃ B + MeS(CH ₂) ₂ O ⁻	156	139 (MeD) 3, 138 (CD ₃ ⁺) 6, 136 (CD ₄) 3, 108 (MeSH) 35, 91 [(CD ₃) ₃ B] 100, 75 (C ₄ H ₄ D ₉ B) 8, 65 (MeSCH ₂ CHO) 15, 63 [MeS(CH ₂) ₂ OD, MeS(CH ₂) ₂ CD ₃] 45, 47 (C ₅ H ₄ D ₉ BO) 16, 43 [(CD ₃) ₃ B + MeSH] 5
Me ₃ B + CD ₃ S(CH ₂) ₂ O ⁻	150	135 (Me ⁺) 3, 134 (CH ₄) 8, 131 (CD ₃ H) 7, 99 (CD ₃ SH) 19, 94 (Me ₃ B) 100, 75 (C ₄ H ₁₀ D ₃ B) 7, 57 (CD ₃ SCH ₂ CHO) 24, 55 [CD ₃ S(CH ₂) ₂ OH] 46, 50 (C ₅ H ₁₃ BO) 18, 43 (Me ₃ B + CD ₃ SH) 4
Me ₃ B + MeSCH ₂ CD ₂ O ⁻	149	134 (Me ⁺) 9, 133 (CH ₄) 28, 100 (MeSD) 34, 93 (Me ₃ B) 100, 77 (C ₄ H ₁₃ B) 10, 58 (MeSCH ₂ CDO) 14, 57 (MeSCH ₂ CD ₂ Me) 12, 55 (MeSCH ₂ CD ₂ OH) 47, 47 (C ₅ H ₁₁ D ₂ BO) 18, 44 (Me ₃ B + MeSD) 5
(CD ₃) ₃ B + 	248	232 (CH ₄) 4 unresolved, 231 (CH ₃ D) 4 unresolved, 216 (MeOH) 24, 183 [(CD ₃) ₃ B] 96, 181 [(CD ₃) ₃ B + H ₂] 17, 151 [(CD ₃) ₃ B + MeOH] 100, 63 [(C ₁₁ H ₁₉)D] 22, 31 (C ₁₃ H ₁₆ D ₉ BO) 3

^a abundance = % with respect to strongest peak.

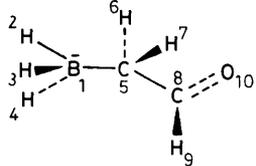
Table 3. Geometries and energies of adducts from $\text{H}_3\text{B} + (\text{CH}_2\text{CHO})^-$.



(10)

–178.58412 au (4.31 G*)
(–235 kJ mol⁻¹ with respect to reactants
considered as 0 kJ mol⁻¹)

Bond length/Å		Bond angle/°	
1–2	1.22	2–1–5	108.6
1–3	1.23	3–1–5	109.9
1–4	1.24	4–1–5	109.9
1–5	1.54	1–5–6	119.0
5–6	1.30	5–6–7	115.7
6–7	1.08	5–6–8	126.0
6–8	1.33	6–8–9	121.1
8–9	1.07	6–8–10	120.4
8–10	1.07	6–5–1–2	179.8
		8–6–5–1	180.1
		7–6–5–8	180.0

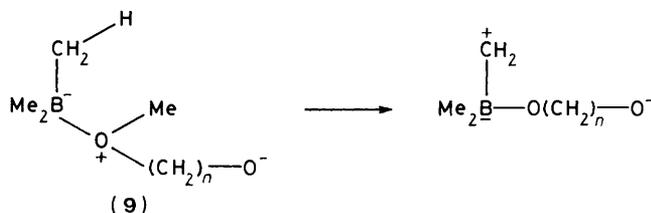


(11)

–178.58270 au (4.31 G*)
(–231 kJ mol⁻¹)

Bond length/Å		Bond angle/°	
1–2	1.23	2–1–5	108.3
1–3	1.24	3–1–5	109.2
1–4	1.23	4–1–5	110.2
1–5	1.69	1–5–8	110.7
5–6	1.09	5–8–9	112.4
5–7	1.09	6–5–8	112.7
5–8	1.48	7–5–8	107.6
8–9	1.10	5–8–10	128.1
8–10	1.20	8–5–1–2	177.7
		10–8–5–1	110.9
		9–8–5–10	181.8

of the saturated side chain, they occur from the alternative adduct (9) (using the particular example $\text{R} = \text{MeO}$). Methane and methanol could be lost by a number of mechanisms from (9). A methane example is shown in Scheme 5; perhaps the



product ion could cyclize in certain cases. We know of no definitive experiment to differentiate between the two possibilities, *i.e.* 'remote' fragmentation or fragmentation through, for example, (9).

Negative ions formed from ambident enolate ions. The possibility of the formation of several types of tetrahedral boron adducts from functionalized alkoxides [*e.g.* (7) and (9)] led us to consider next, the reactions between trimethylborane and enolate ions; ambident species which we expected to react through both C and O.

We have used *ab initio* calculations (4.31 G*)¹⁴ on the simplest model system $\text{H}_3\text{B} + (\text{CH}_2\text{CHO})^-$ to test whether two stable adducts may be formed.* Results are summarized in Table 3, and confirm that deprotonated acetaldehyde (for calculations see ref. 15) may react with H_3B to form the two stable adducts (10) and (11), species which have very similar formation energies. There is no evidence for the existence of a stable species in which both C and O partially bond to boron.

The *c.a.* mass spectra of adducts formed between Me_3B and simple enolates show few peaks, and are listed in Table 4. The fragmentation patterns are illustrated by those of $\text{Me}_3\text{B} +$

* Harmonic analyses were used to identify the authenticity of local minima. We have not carried out high-level calculations on this model system. It is too complex, and we were only interested in whether the two isomers are stable theoretically.

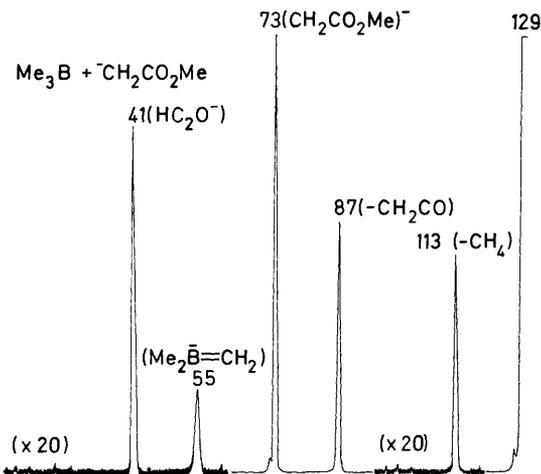
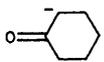


Figure 4. Collisional activation mass spectrum of the addition product(s) formed between Me_3B and $(\text{CH}_2\text{CO}_2\text{Me})^-$.

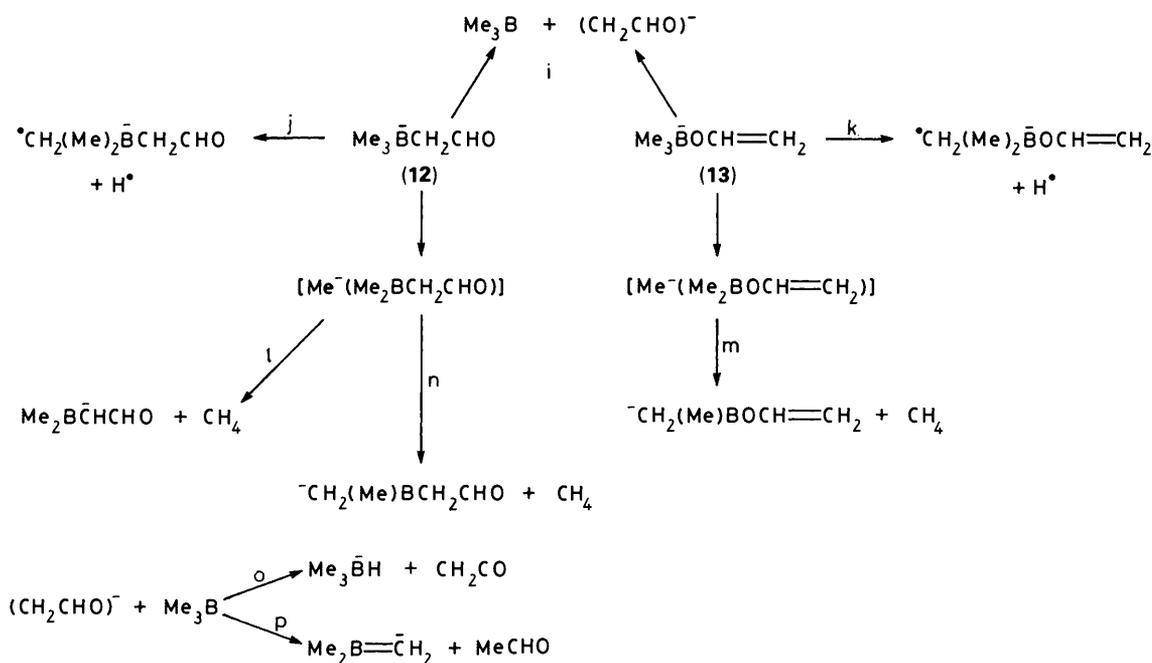
$(\text{CH}_2\text{CHO})^-$, and the interpretation is aided by labelling studies (Table 4). Let us assume, by analogy with the *ab initio* results, that both (12) and (13) (Scheme 6) are present, and that both may fragment independently. Five fragmentations are observed, these are summarized in [pathways (i–p)] (Scheme 6), and show similarities to those outlined in Scheme 2. The major fragmentation gives $(\text{CH}_2\text{CHO})^-$; this could occur from either (12) or (13) [pathway (i)]. Loss of H^+ could occur from either (12) [pathway (j)] or (13) [pathway (k)]. Methane loss involves both methyl and methylene hydrogens. Reactions l–m are possible, but pronounced deuterium isotope effects for these reactions (Table 4) make it difficult to determine which reaction is the major contributor. Two minor reactions are shown *i.e.*, pathway (o) [*cf.* pathway (f)] and pathway (p) [*cf.* pathway (d)]. Other adducts listed in Table 4 behave similarly. The experimental evidence does not allow us to identify or distinguish the individual adducts [*e.g.* (12) or (13)].

The *c.a.* mass spectrum of adducts from Me_3B and deprotonated methyl acetate is shown in Figure 4. The spectra of

Table 4. Collisional activation spectra of adducts formed between Me₃B and various enolate ions (peak heights indicated as % with respect to the strongest peak).

Substrate	Reacting ion ^a	Loss												
		H'	D'	CH ₄	CH ₃ D	CD ₃ H	CD ₄	CH ₂ CO	CD ₂ CO	NuH	NuD	Me ₃ B	(CD ₃) ₃ B	
(CD ₃) ₃ B	⁻ CH ₂ CHO		12					2						100
Me ₃ B	⁻ CD ₂ CHO	15	2	11	4	6	5		1	3				100
Me ₃ B	⁻ CD ₂ CDO	13	2	12	4									100
Me ₃ B	⁻ CH ₂ COMe	8		10										100
Me ₃ B	Et ⁻ CHCOPr	11		9										100
Me ₃ B		7		2										100
Me ₃ B	(MeCO) ₂ CH ⁻	3		3										100
Me ₃ B	⁻ CH ₂ CN	7		9						4				100
(CD ₃) ₃ B	⁻ CH ₂ CN		4			7	3				2			100
Me ₃ B	⁻ CD ₂ CN	8		5	5					4				100
Me ₃ B	⁻ CH ₂ SOMe	3		5						2				100
Me ₃ B	⁻ CD ₂ SOCD ₃	3		2	3					1				100

^a The enolate ion is drawn in the carbanion form merely for ease of representation.

**Scheme 6.**

deuterium labelled derivatives of this system are listed in Table 5, as are those of Me₃B and other deprotonated alkyl acetates. The losses of CH₄, Me₃B and the formation of Me₂B=CH₂ are directly comparable to analogous reactions outlined in Scheme 6. In contrast, the pronounced loss of ketene is not observed for systems listed in Table 4, and may give some insight into the structure of the decomposing adduct in this case. The loss of ketene is observed for all the alkyl acetates studied (Table 5). For the nucleophiles (CH₂CO₂R)⁻, the abundance ratios of peaks resulting from the losses of ketene decrease in the sequence R: Me > Et > Pr > Prⁱ ≈ Bu > Buⁱ (Table 5).

We have shown that deprotonated acetaldehyde should react with H₃B to form stable adducts (10) and (11) (Table 3). Deprotonated methyl acetate should form the corresponding adducts, but may also form a third isomer (15) (Table 6). *ab initio* calculations (Table 6) confirm this species to be a stable structure.* We suggest that ketene loss occurs from (15) (*cf.* (14),

Table 6) as shown in Scheme 7. The observation that the extent of ketene loss is a function of the nature of the alkoxy group (*i.e.* MeO > EtO *etc.*) is compatible with the ability of the deprotonated acetate to form (15) in competition with the other possible adducts. The ability to form (15) is a function of the electron density on the alkoxy oxygen, and that electron density is in turn proportional to the acidity of the corresponding alcohol. Here, Δ*H*_{acid}^o (gas phase) MeOH > EtOH > PrOH > PrⁱOH ≈ BuOH > BuⁱOH,¹⁶ in accord with the trend observed experimentally.

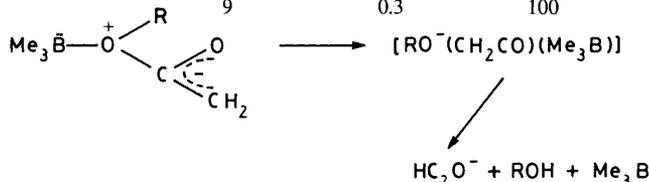
Conclusions

In answer to the three questions outlined in the introduction, we have (i) presented evidence (in simple cases) that nucleophilic

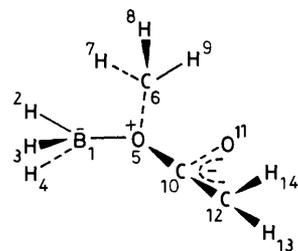
* The size of this system limits us to a low-level calculation (3-21 G).

Table 5. Collisional activation spectra of adducts formed between Me₃B and alkyl acetate enolates (peak heights indicated as % with respect to strongest peak).

Substrate	Reacting ion ≡ Nu	Loss										Formation				
		H ⁺	D ⁺	CH ₄	CH ₃ D	CD ₃ H	CD ₄	CH ₂ CO	CD ₂ CO	NuH	NuD	Me ₃ B	(CD ₃) ₃ B	HC ₂ O ⁻	DC ₂ O ^a	
Me ₃ B	⁻ CD ₂ CO ₂ CD ₃	2		1	1.5							62	1	100		2
Me ₃ B	⁻ CD ₂ CO ₂ Me			1	1.5							60	1	100		2
Me ₃ B	⁻ CH ₂ CO ₂ CD ₃	3		3								68	1	100		
(CD ₃) ₃ B	⁻ CH ₂ CO ₂ Me		1			2.5	1					78			100	3
Me ₃ B	⁻ CH ₂ CO ₂ Et	5		3								28	0.5	100		3
Me ₃ B	⁻ CH ₂ CO ₂ Pr	3		2								15	0.5	100		6
Me ₃ B	⁻ CH ₂ CO ₂ Pr ⁱ	4		5								7	0.2	100		7
Me ₃ B	⁻ CH ₂ CO ₂ Bu	1		2								8	0.3	100		5
Me ₃ B	⁻ CH ₂ CO ₂ Bu ⁱ	1		3								3	0.1	100		4
Me ₃ B	⁻ CH ₂ CO ₂ CH ₂ Ph			2								9	0.3	100		1

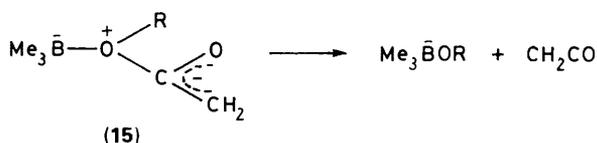


^a The ion HC₂O⁻ could be formed by the process

Table 6.

(14) [-291.01553 a.u. (3-21G)]

Bond length/Å		Bond angle/°	
1-2	1.22	1-5-6	112.5
1-3	1.22	1-5-10	132
1-4	1.21	5-10-11	110
1-5	1.60	5-10-12	110
5-6	1.44	10-12-13	123
6-7	1.08	10-12-14	117
6-8	1.08	6-2-1-3	71
6-9	1.07	7-2-1-3	-97
5-10	1.61	11-10-5-6	-1.5
9-11	2.04	12-7-2-11	180
10-11	1.23		
10-12	1.33		
12-13	1.06		
12-14	1.07		

**Scheme 7.**

addition to an organoborane results in the formation of a structure of tetrahedral geometry, (ii) shown that such structures give characteristic fragmentation patterns when collisionally activated, and (iii) suggested that reaction of Me₃B with a negative ion containing several nucleophilic centres, should, in principle, yield tetrahedral product ions resulting from reaction through each nucleophilic centre. Experimentally, it is often difficult to differentiate between such isomeric structures.

Experimental

C.a. mass spectra were recorded with a VG ZAB 2HF mass spectrometer operating in the negative chemical-ionization mode.¹⁷ All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects. The chemical ionization slit was used in the ion source; ionizing energy 70 eV (tungsten filament); ion source temperature 150 °C; accelerating voltage 7 kV. Reactant HO⁻ ions were formed from H₂O using 70 eV electrons.¹⁸ Alkoxide and enolate precursors were introduced through the septum inlet system at 150 °C. Organoboranes were admitted through a specially constructed gas inlet system at 20 °C. The indicated source pressures were as follows: H₂O (5 × 10⁻⁴ Torr*), enolate or alkoxide precursor (5 × 10⁻⁷ Torr), and borane (5 × 10⁻⁷ Torr). The estimated total source pressure is 10⁻¹ Torr. Alkoxide and enolate ions were formed by reaction of the substrates shown in Tables 1, 2, 4, and 5 with HO⁻. The pressure of He in the second collision cell is 2 × 10⁻⁷ Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of ca. 10% and thus corresponds essentially to single collision conditions.

Trimethylborane¹⁹ and trimethoxyborane²⁰ were prepared by standard methods. [²H₉]Trimethylborane (²H₉ = 99%) was prepared in 75% yield by the reaction between BF₃OEt₂ and CD₃MgI.²¹ The borane ethers Me₂BOMe, Me₂BOCD₃ (²H₃ = 99%), Me₂BOEt, Me₂BOC₂D₅ (²H₅ = 99%) and Et₂BOEt were prepared from either Me₂BBr²² or Et₂BBr²² by reaction with the appropriate alcohol (MeOH, CD₃OD, EtOH, or C₂D₅OD) by a standard route²³ in 70–80% yields.

Preparation of Alcohols.—2-Fluoroethanol, ethylene glycol, and 2-methoxyethan-1-ol were commercial samples. 3-Methoxypropan-1-ol,²⁴ 4-methoxybutan-1-ol,^{25,26} 5-methoxybutan-1-ol,²⁶ 2-dimethylaminoethanol,²⁷ 3-dimethylaminoethanol,²⁷ 2-methylthioethanol²⁸ and 4-methoxycyclohexanol²⁹ were prepared by reported procedures. All these, and subsequent products were checked for purity using ¹H n.m.r. and positive-ion mass spectrometry.

5-Methoxydecahydro-1-naphthol.—To a stirred solution of decahydronaphthalene-1,5-diol (3 g) in anhydrous tetrahydrofuran (100 cm³) under nitrogen was added sodium hydride

* 1 Torr = 133.322 Pa.

(0.35 g), then methyl iodide (1.1 cm³) at 20 °C. The mixture was heated under reflux for 4 h, then allowed to stand at 20 °C for 12 h, the solvent removed *in vacuo*, dichloromethane (100 cm³) was added, and the organic extract washed with aqueous hydrogen chloride (10%, 100 cm³), aqueous sodium chloride (saturated 100 cm³), and dried (Na₂SO₄). Removal of the solvent followed by chromatography of the residue over silicic acid in ethyl acetate–light petroleum (b.p. 40–60 °C 3:2) gave 5-methoxydecahydro-1-naphthol as a colourless liquid (b.p. 120–121 °C/14 mmHg) yield 10% (Found: *M*⁺, 184.1463. C₁₁H₂₀O₂ requires *M*, 184.1457).

The Labelled Compounds.—Incorporation of the label was determined by positive-ion mass spectrometry. [*O,O'*-²H₂]-Ethylene glycol was prepared by exchange with D₂O in the septum inlet (at 150 °C) of the mass spectrometer.

[1,1-²H₂]-2-Fluoroethanol. A mixture of ethyl fluoroacetate (0.42 g), lithium aluminium deuteride (0.1 g) in diethyl ether (4 cm³) was heated under reflux for 1 h, cooled (to 20 °C), aqueous sodium hydroxide (10%, 0.5 cm³) was added, the ethereal phase separated and distilled to yield [1,1-²H₂]-2-fluoroethanol (0.18 g, 70%); b.p. 102–103 °C/760 mmHg. ²H₂ = 98%.

[1,1-²H₂]-2-Methoxyethanol. Methyl 1-methoxyacetate (0.52 g) was added dropwise at 20 °C and under nitrogen to a stirred suspension of lithium aluminium deuteride (0.12 g) in anhydrous diethyl ether (5 cm³). The mixture was heated under reflux for 1 h, cooled to 20 °C, aqueous sodium hydroxide (10%, 0.25 cm³) was added, the mixture filtered, and [1,1-²H₂]-2-methoxyethanol (0.34 g, 88%) was collected by distillation (124–125 °C/760 mmHg). ²H₂ = 98%.

[MeO-²H₃]-2-(Methoxy)ethanol. A mixture of sodium (0.16 g), [²H₄]-methanol (0.25 g) 2-chloroethanol (0.56 g) and anhydrous tetrahydrofuran (5 cm³) was heated in a sealed glass tube at 80 °C for 1 h. On being cooled to 20 °C, the mixture was filtered, and the filtrate distilled to give 2-([²H₃]methoxy)ethanol (0.41 g, 74%), b.p. 124–125 °C/760 mmHg. ²H₃ = 99.5%.

[1,1-²H₂]-3-Methoxypropanol. This was prepared as for [1,1-²H₂]-2-methoxyethanol (above) except that methyl 3-methoxypropanoate was used. Yield 91%, b.p. 152–154 °C/760 mmHg. ²H₂ = 98%.

[1,1-²H₂]-2-Dimethylaminoethanol. This was prepared from Me₂NCH₂CO₂Et by the same method used for [1,1-²H₂]-2-fluoroethanol (²H₂ = 98%).

[Me,Me'-²H₆]-2-Dimethylaminoethanol. A mixture of 2-aminoethanol (0.23 g), triethylamine (1.6 cm³) and [²H₃]-iodomethane (0.5 cm³) was heated under reflux for 3 h. The mixture was cooled to 20 °C, filtered, and the filtrate distilled to yield [Me,Me'-²H₆]-2-(dimethylamino)ethanol (0.13 g, 37%), b.p. 133–134 °C/760 mmHg. ²H₆ = 99%.

[1,1-²H₂]-2-Methylthioethanol. This was prepared from MeSCH₂CO₂Et by the same method used for 1,1-²H₂]-2-fluoroethanol (²H₂ = 98%).

[MeS-²H₃]-2-Methylthioethanol. A mixture of potassium *t*-butoxide (0.18 g), 2-mercaptoethanol (0.11 cm³) [²H₃]iodomethane (0.10 g) and anhydrous tetrahydrofuran was heated under reflux for 1 h. The reaction mixture was filtered, and distillation gave [MeS-²H₃]-2-methylthioethanol (0.13 g, 87%), b.p. 169–171 °C/760 mmHg. ²H₃ = 99%.

Preparation of Enolate Precursors.—Acetaldehyde, [²H₄]-acetaldehyde, acetone, cyclohexanone, acetyl acetone, acetonitrile, [²H₃]acetonitrile, dimethyl sulphoxide, [²H₆]dimethyl sulphoxide, methyl acetate, and ethyl acetate were commercial samples. All other alkyl acetates are known and were prepared by a reported procedure.³¹ [²H₃]Acetaldehyde, [²H₃]methyl acetate, [²H₆]methyl acetate were prepared by exchange of acetaldehyde, methyl acetate and [²H₃] methyl acetate with MeOD.

Conditions: Substrate (1 g), MeOD (25 g), reflux under

nitrogen for 4 h: ²H₃ ≥ 80% in all cases. [²H₃]Methyl acetate was prepared by the reaction of acetyl chloride with [²H₄]methanol.³¹

Acknowledgements

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