Collision Induced Dissociations of Carbanions in the Gas Phase: the Formation of Vinylidene Carbene Intermediates from Deprotonated Prop-2-ynyl Ethers

Suresh Dua, John H. Bowie and John C. Sheldon
Department of Chemistry, The University of Adelaide, South Australia, 5005

Evidence is presented which suggests that the anionic isomers $MeO{-}CH_2{-}C{\equiv}C^-$ and $CH_2{=}C{=}C^-{-}OMe$, upon collision activation in the gas phase, fragment through the vinylidene carbene intermediate $[(CH_2{=}C{=}C{:})MeO^-]$. In particular, the intermediate eliminates CH_2O and MeOH to form $C_3H_3^-$ and C_3H^-, respectively. *Ab initio* calculations indicate that the latter ion has a ground state triplet structure with 'allenic' type geometry.

The fragmentations of even-electron organic anions mainly involve the loss of neutral molecules. Such reactions normally involve the charged site, either directly or following proton transfer to that site. Fragmentation 'rules' have been described; the fragmentations are usually predictable and simple, but rearrangement reactions have also been reported.[1-3] Radical loss is also observed, but only when a stabilised radical anion may be formed.[4]

We are currently examining anions where the simple fragmentation 'rules' might not pertain. We expected deprotonated prop-2-ynyl ether $[MeO{-}CH_2{-}C{\equiv}C^-]$ to fall into this category. Simple fragmentation seems unlikely because the anion centre appears to be 'blocked' by the triple bond, and proton transfer to form a decomposing species $[MeO{-}{}^-CH{-}C{\equiv}CH]$ [which should readily lose $Me^{\bullet}$ to form $(O{=}CH{-}C{\equiv}CH)^{\bullet-}$ (*cf.* ref. 4)] must be energetically unfavourable. What type of fragmentation do such systems undergo? Could they, for example, rearrange in some way prior to fragmentation, or might they perhaps undergo some process which occurs remote from and uninfluenced by the charged centre (a 'remote' fragmentation[5,6])?

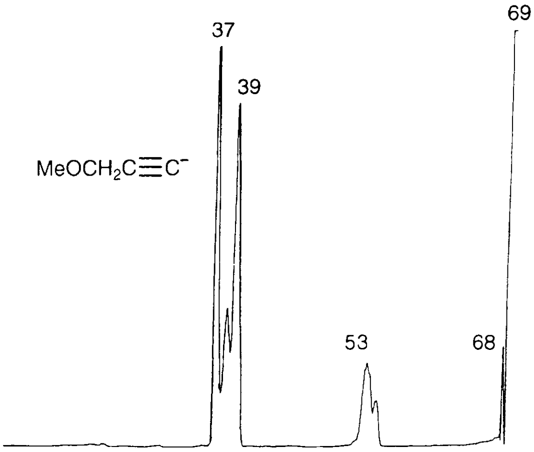
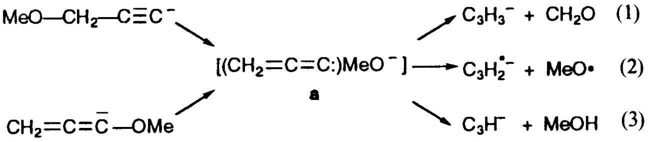


Fig. 1 Collisional activation mass spectrum (MS/MS) of $MeO{-}CH_2{-}C{\equiv}C^-$. The ion is formed by the reaction of $MeO{-}CH_2{-}C{\equiv}CD$ with HO^-. Recorded with a ZAB 2HF mass spectrometer; for operating conditions, see Experimental. The CA mass spectrum of the isomeric ion $CH_2{=}C{=}C^-{-}OMe$ (formed by reaction of $CH_2{=}C{=}CD{-}OMe$ with HO^-) is as follows [*m*/*z* (loss) abundance]: 68 ($H^{\bullet}$, 32%), 54 ($Me^{\bullet}$) 100, 53 (CH_4) 8, 39 (CH_2O) 15, 38 ($MeO^{\bullet}$) 7, 37 (MeOH) 14. The peaks *m*/*z* 39, 38 and 37 are insufficiently resolved to allow comparison of individual peak widths with those shown in Fig. 1. The major fragmentation in this case occurs by the process $CH_2{=}C{=}C^-{-}OMe \rightarrow (CH_2{=}C{=}C{=}O)^{\bullet-} + Me^{\bullet}$.]



Scheme 1

Results and Discussion

The collisional activation mass spectrum (CA MS/MS) of the $(M - D)^-$ ion from $MeO{-}CH_2{-}C{\equiv}C{-}D$ is recorded in Fig. 1; the major peaks at *m*/*z* 37, 38 and 39 are formed by losses of MeOH, $MeO^{\bullet}$ and CH_2O, respectively, from the parent anion. This is an unusual and unexpected result from this system; there appears to be no reported precedent for such behaviour in the gas phase. What, then, are the mechanisms of such processes? It is of interest in this context that base catalysis of (the related) 3-chloro-3-methylbut-1-yne in solution has been shown to proceed through the intermediacy of vinylidene carbene $[Me_2C{=}C{=}C{:}]$ in the rate determining step of the reaction.[7] This could well be the clue to the mechanistic problem. If a similar mechanism operates in the gas phase, then the product ions might be formed through the vinylidene carbene–methoxide anion intermediate **a** as summarised in Scheme 1. In order to probe this proposal, we have attempted to prepare intermediate **a** by an unambiguous and independent route, *viz.* by α-cleavage of $CH_2{=}C{=}C^-{-}OMe$. The collision induced mass spectrum of the $(M - D)^-$ ion from $CH_2{=}C{=}CD{-}OMe$ is recorded in the legend to Fig. 1; it also contains *m*/*z* 37, 38 and 39. Thus, we propose the formation of a common vinylidene carbene–methoxide anion intermediate as summarised in Scheme 1. Reactions (1) and (3) are of particular interest. The methoxide ion is known to be a hydride transfer reagent.[8] In principle, provided that MeO^- is loosely bound in **a**, the hydride ion transfer of reaction (1) could occur (i) to the electron deficient carbene centre of intermediate **a** to form the prop-2-ynyl anion, $^-CH_2{-}C{\equiv}CH$, or (ii) to the electrophilic centre of the zwitterionic contributor (*i.e.* $^+CH_2{-}C{\equiv}C^-$) of the neutral component in **a** to form the methyl acetylide ion $MeC{\equiv}C^-$. This matter is resolved by a comparison of the charge reversal (positive ion) mass spectra[9] of authentic $MeC{\equiv}C^-$ and $^-CH_2C{\equiv}CH$ (Fig. 2) with those (Fig. 3) of the ions with *m*/*z* 39 formed from the isomers $CH_2{=}C{=}C^-{-}OMe$ and $MeOCH_2{-}C{\equiv}C^-$. The results are quite dramatic. The $C_3H_3^-$ ion from the allenyl isomer corresponds exclusively to the prop-2-ynyl anion $^-CH_2C{\equiv}CH$ [Fig. 3(*a*)],* whereas *m*/*z* 39 from deprotonated

---

* This is an interesting result, since addition of HNu to $Me_2C{=}C{=}C{:}$ in solution gives $Me_2C(Nu){-}C{\equiv}CH$, presumably through the zwitterionic structure $R^1R^2C^+{-}C{\equiv}C^-$.[7] That the opposite occurs for the gas phase addition of H^- to $CH_2{=}C{=}C{:}$ may be a direct consequence of a lesser zwitterionic contribution in this case (Me stabilises the adjacent positive charge more than H), which could result in a specific orientation effect within the complex, delivering H^- to the carbene centre. We are unable to compare this result with the analogous reaction from $[(Me_2C{=}C{=}C{:})MeO^-]$, since loss of CH_2O is much reduced in this system (see Table 2).

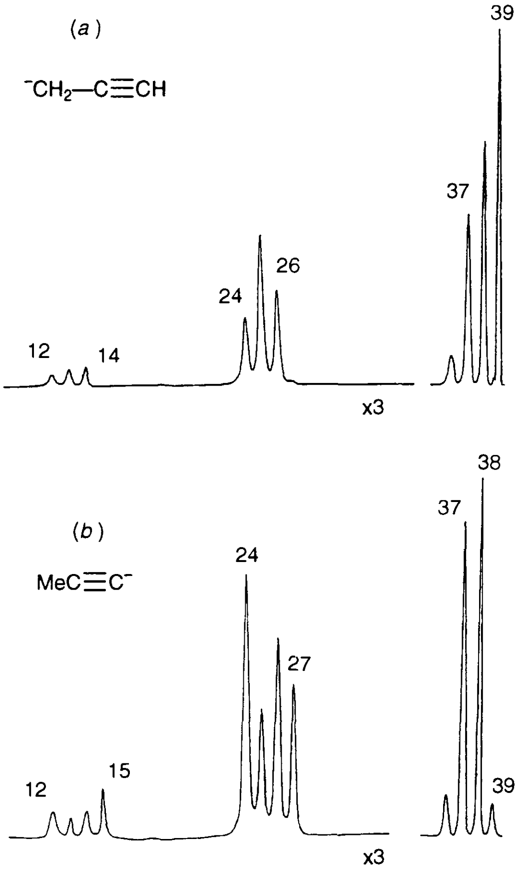


Fig. 2 Charge reversal (positive ion) mass spectra[9] of (a) $^-CH_2C{\equiv}CH$ (formed by deprotonation of allene with HO^-) and (b) $MeC{\equiv}C^-$ [formed by a standard[10] S_N2(Si) reaction between $Me_3SiC{\equiv}CMe$ and HO^-]

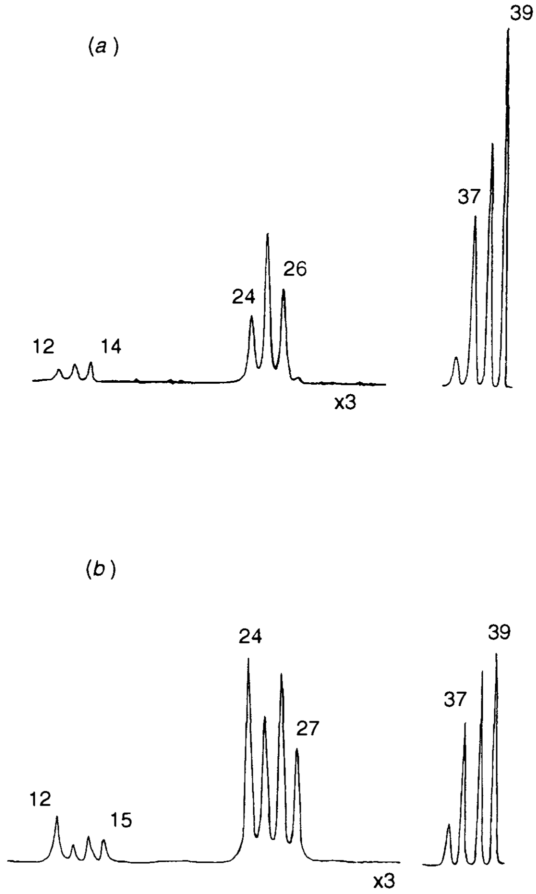
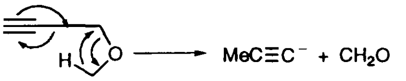


Fig. 3 Charge reversal (positive ion) mass spectra of the $C_3H_3^-$ ions from (a) $CH_2{=}C{=}C^-{-}OMe$ and (b) $MeOCH_2C{\equiv}C^-$

prop-2-ynyl methyl ether is a mixture of $^-CH_2C{\equiv}CH$ and $MeC{\equiv}C^-$ [Fig. 3(b)]. Thus we propose that the prop-2-ynyl anion from the acetylenic isomer is formed from the vinylidene carbene intermediate **a**. However, the methyl acetylide anion must arise by a different route; perhaps by the concerted reaction (4) of Scheme 2.



$$MeC{\equiv}C^- + CH_2O \qquad (4)$$

Scheme 2

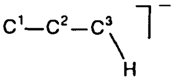
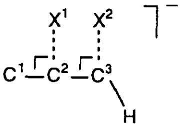
The ion formed by loss of methanol [Scheme 1, reaction (3)] has the formula C_3H^-. *Ab initio* calculations (at HF/6–311 + + G** level) of possible C_3H^- structures have been carried out, and are summarised in Table 1. These indicate that the hydrogen is attached to a terminal carbon; structures containing the hydrogen on the central hydrogen are unstable. There are two ground state C_3H^- ions: one is a singlet species, best represented by the formulation $^-C{\equiv}C{-}\ddot{C}{-}H$, but the more stable ion (by 15 kJ mol^{-1} at CID/6–311G+ +G**//HF/6–311+ +G** level of theory) is a triplet. The closest valence bond representation of this triplet is $^-\dot{C}{=}C{=}\dot{C}{-}H$ [*cf.* the C=C bond length of 1.305 Å (Table 1) with that of allene (1.309 Å)]. However, this simplistic description does not deal appropriately with the two unpaired electrons. In molecular orbital terms, the two unpaired electrons occupy the two lowest antibonding and orthogonal π-orbitals which extend along the carbon chain. Most of the spin density (1.86) is concentrated on the carbon which bears hydrogen.

The proposal of the formation of a vinylidene carbene–methoxide intermediate seems reasonable in view of the results outlined above, and there thus seems to be no reason to invoke the possibility either of skeletal rearrangement preceding fragmentation or a high energy 'remote' fragmentation (*e.g.* a four-centre elimination of methanol which does not involve the charged centre). It is now of interest to investigate related systems which also might decompose *via* vinylidene carbene–alkoxide ion complexes $[(R^1R^2C{=}C{=}C\!:)RO^-]$ (where R^1 and R^2 = H, Me and R = Me, Et), and we have chosen ions $(RO)R^1R^2C{-}C{\equiv}C^-$ as precursors for this purpose. The mass spectra of the acetylenic precursor anions together with those of some deuteriated analogues are listed in Table 2. The spectra of a product ion in one of these spectra are recorded in Table 3. Methyl and ethyl ethers behave similarly; we use the methyl ethers as examples in the discussion below.

The loss of methanol is the dominant fragmentation of $(MeO)MeCH{-}C{\equiv}C^-$: losses of MeO• and CH_2O (*cf.* Scheme 1) are now minor in comparison. The spectra of the two labelled derivatives shown in Table 2 show that there are two competing and comparable losses of methanol. We propose that both occur from intermediate **b** by the processes shown in eqns. (5) and (6) (Scheme 3). Whether the carbenoid anion **c** [eqn. (6)] is stable or undergoes rearrangement to a more stable isomer is not known. There are two other fragmentation processes that are also of particular interest in this spectrum, *viz.* the losses of CH_4 and H_2. Labelling data (Table 2) establish the atoms involved in these losses, and we propose that the processes are best rationalised by fragmentation through vinylidene carbene–hydride ion complex **d**. The reactions are depicted respectively as an S_N2 process [eqn. (7)] and a deprotonation [eqn. (8)].

Finally, the majority of the fragmentations of $Me_2(MeO)C{-}C{\equiv}C^-$ are similar to those outlined in Scheme 3. The spectrum (Table 2) is again dominated by loss of methanol, but in this

Table 1 *Ab initio* calculations on C_3H^- (GAUSSIAN 86[11])[a]

	Singlet state (C_s symmetry) 	Triplet state (C_1 symmetry)[b] 
Bond length (Å)		
C(1)–C(2)	1.264 3	1.305
C(2)–C(3)	1.345 8	1.305
C(3)–H	1.098 7	1.068
Bond angles or dihedral angle (°)		
C(1)–C(2)–C(3)	176.8	174.1
C(2)–C(3)–H	108.8	141.7[c]
C(1)–C(2)–X(1)–C(3)		180.2
C(2)–C(3)–X(2)–H		178.6
Energy (E_h)[d]		
(HF/6–311 + +G**)	−114.026 56	−114.058 68
(CID/6–311G**//HF/6–311 + +G**)	−114.363 51	−114.369 14

[a] The electronic structures were computed by the *ab initio* LCGOMO method for the lowest energy states of C_3H^- as singlet and triplet (diradical). The geometries of these states were fully optimised at the HF/6–311 + +G** level. Energies were also computed by extending the wavefunction by configuration interaction (CID/6–311G**//HF/6–311 + +G**). [b] The dummy atoms X(1) and X(2) define dihedral intersections. [c] This large angle reflects the open shell and lack of trigonal electron pairs on C(3). [d] 1 E_h = 2625.500 kJ mol^{-1}.

Table 2 Collisional activation mass spectra of $(RO)R^1R^2C–C{\equiv}C^-$ species and some deuteriated analogues

Precursor ion (*m/z*)	*m/z* (loss or formation) relative abundance
$[EtOCH_2–C{\equiv}CH - H]^-$ (83)	82 ($H^{\bullet}$) 12%, 53 (C_2H_6) 12, 39 (MeCHO) 100, 38 ($EtO^{\bullet}$) 18, 37 (EtOH) 78, 25 (C_2H^-) 5
$[(MeO)MeCH–C{\equiv}CH - H]^-$ (83)	82 ($H^{\bullet}$) 15%, 81 (H_2) 8, 67 (CH_4) 7, 53 (CH_2O) 37, 52 ($MeO^{\bullet}$) 32, 51 (MeOH) 100, 31 (MeO^-) 1
$[(MeO)MeCD–C{\equiv}CH - H]^-$ (84)	83 ($H^{\bullet}$) 12%, 82 ($D^{\bullet}$) 6, 83 (HD) 8, 67 (CH_3D) 8, 54 (CH_2O) 37, 53 ($MeO^{\bullet}$) 39, 52 (MeOH) 100, 51 (MeOD) 54, 31 (MeO^-) 1
$[(CD_3O)MeCH–C{\equiv}CH - H]^-$ (86)	85 ($H^{\bullet}$) 8%, 84 (H_2) 4, 67 (CD_3H) 9, 54 (CD_2O) 15, 52 ($CD_3O^{\bullet}$) 14, 51 (CD_3OH) 100, 34 (CD_3O^-) 1
$[(EtO)MeCH–C{\equiv}CH - H]^-$ (97)	96 ($H^{\bullet}$) 15%, 82 ($Me^{\bullet}$) 1, 67 (C_2H_6) 18, 53 (MeCHO) 32, 52 ($EtO^{\bullet}$) 10, 51 (EtOH) 100, 45 (EtO^-) 3, 43 ($CH_2{=}CHO^-$) 1, 25 (C_2H^-) 2
$[(MeO)Me_2C–C{\equiv}CD - D]^-$ (97)	96 ($H^{\bullet}$) 2, 67 (CH_2O) 8, 66 ($MeO^{\bullet}$), 18,[a] 65 (MeOH) 100
$[(EtO)Me_2C–C{\equiv}CH - H]^-$ (111)	110 ($H^{\bullet}$) 1, 67 (MeCHO) 7, 65 (EtOH) 100, 45 (EtO^-) 2, 43 ($CH_2{=}CHO^-$) 1, 25 (C_2H^-) 1

[a] Unresolved.

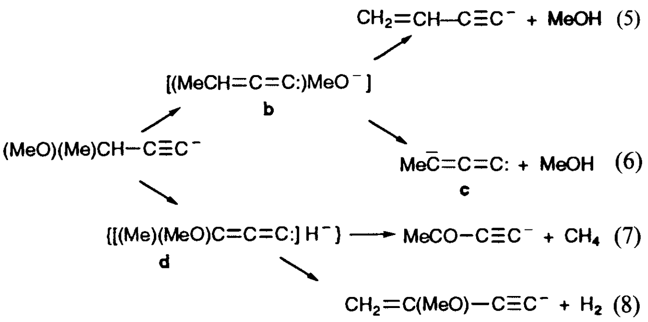
Table 3 Spectrum of the $C_5H_5^-$ product ion from $(MeO)Me_2C–C{\equiv}C^-$

Product ion (*m/z*)	Spectrum type	CA spectrum: *m/z* (loss) abundance CR spectrum: *m/z* (abundance)[a]
$C_5H_5^-$ (65)	CA	64 ($H^{\bullet}$) 100%, 63 (H_2), 24, 50 ($Me^{\bullet}$) 8, 25 (C_2H^-) 2
	CR	65(78%), 64(38), 63(94), 63(94), 62(54), 61(32), 60(2), 52(7), 51(28), 50(84), 49(75), 48(15), 40(6), 39(100), 38(59), 37(64), 36(21), 27(18), 26(15), 24(14), 15(2), 14(1), 13(1), 12(2)
$CH_2{=}C(Me)C{\equiv}C^-$ (65)	CA[b]	64($H^{\bullet}$) 100%, 63 (H_2) 25, 50 ($Me^{\bullet}$) 8, 25 (C_2H^-) 3
	CR[b]	65(75%), 64(36), 63(91), 62(58), 61(38), 60(3), 52(6), 51(30), 50(85), 49(79), 48(18), 40(5), 39(100), 38(60), 37(61), 36(20), 27(18), 26(12), 25(12), 24(13), 15(3), 14(2), 13(1), 12(2)

[a] Charge reversal (positive ion) mass spectrum.[9] [b] It is of interest to compare these spectra with those of the cyclopentadienyl anion: CA MS/MS 64($H^{\bullet}$) 100%, 39 (C_2H_2) 5; CR MS/MS 65(100%), 64(54), 63(78), 62(25), 61(15), 60(2), 51(7), 50(17), 49(12), 39(21), 38(36), 37(26), 36(8), 27(1), 26(10), 25(4).

case, the product ion is exclusively $CH_2{=}C(Me)–C{\equiv}C^-$ [*cf.* eqn. (4) (Scheme 2)]. This ion has been identified by comparison of its spectra (Table 3) with those of an authentic species.

In conclusion, we propose that deprotonated prop-2-ynyl ethers fragment *via* vinylidene carbene intermediates by the scenarios outlined in Schemes 1 and 3. Such intermediates may



Scheme 3

undergo a number of reactions, including dissociation, hydride transfer, deprotonation and S_N2 processes.

Experimental

Collisional activation (CA) and charge reversal (CR, positive ion)[9] mass spectra (MS/MS) were determined with a VG ZAB 2HF instrument. Full experimental details have been reported previously.[12] Specific details were as follows: a chemical ionization slit was used in the ion source, the ionizing energy was 70 eV, the ion source temperature was 50 °C, and the accelerating voltage was 7 kV. Liquids were introduced through the septum inlet at 50 °C (pressure of sample 5×10^{-7} Torr).* Deprotonation was effected using HO^- (from H_2O; source pressure 1×10^{-5} Torr). The estimated source pressure was 10^{-1} Torr. Argon was used in the second collision cell (measured pressure, outside the cell, 2×10^{-7} Torr), giving a 10% reduction in the main beam, equivalent to single collision conditions.

2-Methylbut-1-en-3-yne and prop-2-ynyltrimethylsilane were commercial samples. The following compounds were prepared by reported procedures: allene,[13] 3-methoxyprop-1-yne,[14] 3-ethoxyprop-1-yne,[15] 3-methoxybut-1-yne,[16] 3-ethoxybut-1-yne,[15] 3-methoxy-3-methybut-1-yne,[17] 3-ethoxy-3-methylbut-1-yne[17] and 1-methoxyallene.[18]

The Labelled Compounds.—[1-^{2}H]-1-Methoxyallene was prepared by a reported method[19] (99% ^{2}H). The three 1-^{2}H acetylenic compounds were made as follows.

[1-^{2}H]-3-*Methoxy*-3-*methylbut*-1-*yne*. To a solution of 3-methoxy-3-methylbut-1-yne (1 g) in anhydrous diethyl ether (20 cm^3), was added a mixture of methyllithium in diethyl ether (7.5 cm^3; 1.4 mol dm^{-3}) dropwise at −78 °C, and the mixture was stirred at that temperature for 30 min. Deuterium oxide (0.5 cm^3) was added, and the system was allowed to warm to 25 °C. Fractional distillation gave the required product in 80% yield (99% ^{2}H).

3-([$^2H_3$]*Methoxy*)*but*-1-*yne*. To a suspension of sodium hydride (0.5 g, 80%, prewashed with anhydrous hexane) in anhydrous diethyl ether (20 cm^3) was added, dropwise and at 0 °C, a solution of but-3-yn-2-ol (1 g) in anhydrous diethyl ether (5 cm^3). The mixture was stirred at 0 °C for 30 min, at 25 °C for 1 h and was then cooled to 0 °C. [$^2H_3$]Methyl iodide (1 cm^3) was added and the mixture heated under reflux for 24 h, then cooled to 0 °C. Water (5 cm^3) was added, and the organic layer was separated and dried (Na_2SO_4). Removal of the solvent, followed by fractional distillation, gave the product (0.45 g, 40%, 99% $^2H_3$), b.p. 62–63 °C/760 mmHg.

[3-^{2}H]-3-*Methoxybut*-1-*yne*. Sodium borodeuteride (0.4 g) was added at 0 °C to a mixture of but-3-yn-2-one[20] (2 g), deuterium oxide (2 cm^3) and anhydrous tetrahydrofuran (30 cm^3), and the mixture was stirred first at 0 °C for 30 min, then for 24 h at 25 °C. After cooling to 0 °C, aq. ammonium chloride (saturated, 5 cm^3) was added, the mixture was extracted with diethyl ether (25 cm^3), and the organic phase was separated and dried (Na_2SO_4). Removal of the diethyl ether followed by fractional distillation gave [2-^{2}H]but-3-yn-2-ol (1.4 g, 70%), which was methylated by a reported procedure[16] to yield the product in overall 80% yield (99% ^{2}H).

Acknowledgements

We thank the Australian Research Council for financial support. One of us (S. D.) thanks the ARC for the award of a research associate position.

References

1 J. H. Bowie, *Mass Spectrom. Rev.*, 1990, **9**, 349.
2 J. H. Bowie, *Org. Mass. Spectrom.*, in the press.
3 S. Dua, P. C. H. Eichinger and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, in the press.
4 P. C. H. Eichinger and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, 1991, **110**, 123.
5 J. Adams, *Mass Spectrom. Rev.*, 1990, **9**, 142.
6 M. L. Gross, *Int. J. Mass Spectrom. Ion Processes*, 1992, **118–119**, 137.
7 H. D. Hartzner, in *Carbenes*, eds. R. A. Moss and M. Jones, Wiley, New York, 1975, vol. 2, pp. 73–84, and refs. cited therein.
8 S. Ingemann, T. C. Kleingeld and N. M. M. Nibbering, *J. Chem. Soc., Chem. Commun.*, 1982, 1009.
9 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; J. E. Szulejko, J. H. Bowie, I. Howe and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **34**, 98.
10 C. H. DePuy, R. Damrauer, J. H. Bowie and J. C. Sheldon, *Acc. Chem. Res.*, 1987, **20**, 127.
11 M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. J. P. Steward, F. W. Bobrowicz, C. M. Rohlfing, L. R. Khan, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder and J. A. Pople, GAUSSIAN 86, Carnegie–Mellon Quantum Chemistry, Pittsburg, PA, 1984.
12 M. B. Stringer, J. H. Bowie and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
13 H. N. Cripps and E. F. Kiefer, *Org. Syn.*, 1973, coll. vol. 5, 22.
14 W. Reppe, *Liebigs Ann. Chem.*, 1955, **596**, 1.
15 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, New York, 1971, 172.
16 D. Guillerm-Dorn and M. L. Capman, *Bull. Soc. Chim. Fr.*, 1973, 1417.
17 E. J. Corey, D. Floyd and B. H. Lipshutz, *J. Org. Chem.*, 1978, **43**, 3418.
18 F. J. Weiberth and S. S. Hall, *J. Org. Chem.*, 1985, **50**, 5308.
19 S. Hoff, L. Brandsma and J. F. Areus, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 1179.
20 B. Heilbron and J. Weedon, *J. Chem. Soc.*, 1946, 39.

Paper 3/05202H
Received 31*st August* 1993
Accepted 25*th October* 1993

---

* 1 Torr ≈ 133.322 Pa.