# The Gas-phase Wittig–Oxy Cope Rearrangement of Deprotonated Diallyl Ether

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Collisional activation of deprotonated diallyl ether is found to give major products formed by competitive losses of H_2, C_3H_4O and C_4H_6. Products are rationalised in terms of the Wittig-oxy Cope rearrangement sequence $CH_2=CH-\bar{C}H-O-allyl \longrightarrow (CH_2=CH)(CH_2=CH-CH_2)CHO^- \longrightarrow CH_2=CH(CH_2)_2\dot{C}HCHO \longrightarrow$ products. The spectrum of $CH_2=CH-\bar{C}DOCD_2CH=CH_2$ shows the operation of both 1,2- and 1,4-Wittig rearrangements, while that of $CH_2=CH-\bar{C}DO-allyl$ shows proton transfer (to form $CH_2=CH-CHD-O-\bar{C}HCH=CH_2$) to be a minor process.

One of the better known carbanion rearrangements in the condensed phase is the Wittig rearrangement.[1-3] The rearrangement can, in principle, involve either of the intermediates shown in Scheme 1, and to support such mechanistic proposals it has been shown that aldehydes are often by-products of the reaction.[4,5] The migratory aptitude of substituent R^1 is allyl $\simeq$ benzyl > methyl > ethyl > phenyl,[4,5] and since this is the order of free-radical stabilities,[6,7] it has been suggested[8] that the radical pair mechanism is the more likely.
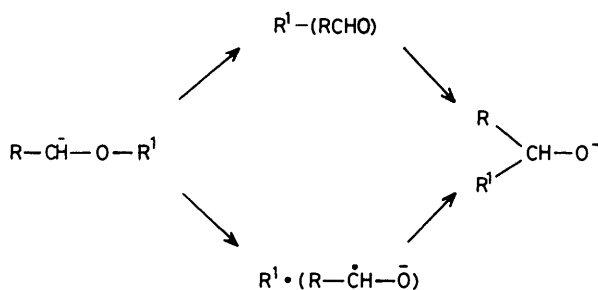

Scheme 1.

The collisional activation (CA) mass spectra of ions PhCHOR and Ph(R)CH-O⁻ (R = alkyl and phenyl) are very similar, suggesting that the Wittig rearrangement also occurs in the gas phase.[9] Major fragmentations are best interpreted in terms of decomposition of the Wittig product ion. For example, Ph$\bar{C}$HOEt converts into Ph(Et)CHO⁻ and this ion undergoes the processes shown in equations (1) and (2), with the latter process involving prior scrambling of phenyl hydrogens. An analogous process, $Ph_2CH-O^- \longrightarrow (C_6H_4)^-CHO + C_6H_6$, gives the major peak in the spectrum of 'Ph-$\bar{C}$H-O-Ph'.

$$(C_6H_4)^-CHO + C_2H_6 \quad (2) \qquad MeCH=CHO^- + C_6H_6 \quad (1)$$
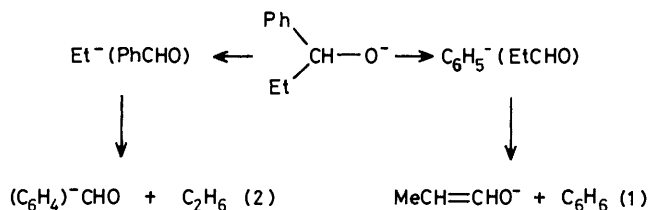
In the condensed phase, treatment of diallyl ether with KNH_2-NH_3 gives hexa-1,5-dien-3-ol by a Wittig rearrangement,[10,11] and, on heating, this alcohol yields hex-5-en-1-al via an oxy Cope rearrangement.[12] In this paper we investigate the problem of whether deprotonated diallyl ether may undergo Wittig followed by oxy Cope rearrangements in the gas phase.

Three questions are addressed: (i) do ions (a) and (b) interconvert by proton transfer? (ii) does ion (a) undergo a Wittig rearrangment to (c) and if so is this a 1,2- or 1,4-rearrangement? (iii) if the Wittig rearrangement forms (c) does (c) rearrange to (d) by an anionic oxy Cope[13] reaction?
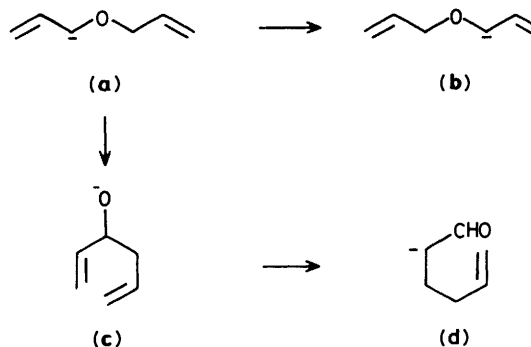
Results and Discussion

Full experimental details are provided in the Experimental section. CA mass spectra are either illustrated in Figures 1 and 2 or listed in Table 1. Charge reversal (positive ion) mass spectra of negative ions[14] are recorded in Table 2.

The CA mass spectra of the $(M - H^+)^-$ ions (a), (c), and (d) of diallyl ether, hexa-1,5-dien-3-ol, and hex-5-en-1-al are recorded in Figure 1, Table 1, and Figure 2, respectively. The spectra are very similar; in particular, the half heights of the corresponding peaks in each spectrum are, within experimental error, the same (see legends to Figures 1 and 2, also footnote *b* in Table 1). It is likely that all three systems are decomposing through a common ion. We suggest that this ion is (d) and that it is formed by Wittig rearrangement (a) $\longrightarrow$ (c) followed by the oxy Cope rearrangement (c) $\longrightarrow$ (d). The charge-reversal spectra of the $(M - H^+)^-$ ions of diallyl ether, hexa-1,5-dien-3-ol, and hex-5-en-1-al are recorded in Table 2. They show the same peaks, but the peak abundances are significantly different in each case. We may therefore conclude that the rearrangements (a) $\longrightarrow$ (c) $\longrightarrow$ (d) occur (at least in part) after collision activation of ions (a) and (c).†

† Since m/z 43 and 41 (Figure 1) are formed, in part, by unimolecular processes (see legend to Figure 1), the rearrangement (a) to (d) also occurs in the ion source. A quantitative statement concerning the relative proportion of rearrangement occurring in the source and after collisional activation cannot be made.

Table 1. Major product peaks in the CA mass spectra of diallyl ether and related species

Compd.	Initial ion	-H₂	-HD	C₃H₅⁻ (m/z 41)	C₃H₄D⁻ (42)	C₃H₃D₂⁻ (43)	⁻CH₂CHO (43)	⁻CH₂CDO/⁻CHDCHO (44)	⁻CHDCDO (45)
(CH₂=CHCD₂)₂O	CH₂=CH-C̄DOCD₂CH=CH₂	18	18				100	33	24
CH₂=CHCD₂O allyl	CH₂=CH-C̄HOCD₂CH=CH₂	18	15		4	100ᵃ	a	22	
	CH₂=CH-C̄DOCH₂CH=CH₂ (Ō)	24	11	100	9		4	72	
allyl CH(CH=CH₂)OH	CH₂=CH-C̄H-CH₂CH=CH₂ ᵇ	25		100			36		
CH₂=CH(CH₂)₃CHO	CH₂=CH(CH₂)₂C̄HCHO	28		100			33		
CH₂=CH-(CH₂)₂CD₂CHO	CH₂=CH(CH₂)₂C̄DCHO	21	3	100				38	

ᵃ C₃H₃D₂⁻ and ⁻CH₂CHO are both 43 atomic mass units (a.m.u.). Since ⁻CH₂CHO and C̄HDCHO (m/z 44, 22% abundance) arise from the respective 1,2- and 1,4-rearrangements of CH₂=CH-C̄HOCD₂CH=CH₂ (cf. Scheme 3), at least 22% (and probably more) of m/z 43 must correspond to ⁻CH₂CHO. ᵇ The voltages at half height of the main peaks are [m/z (volts ± 0.3)]; 95 (59.7), 43 (49.1), and 41 (34.1).

Table 2. Charge-reversal spectra of negative ions

Ion	m/z	13	14	26	27	29	39	41	51	53	55	57	63	65	67	69	77
CH₂=CH-C̄HO-allyl		2	2	19	46	40	100	71	23	38	16	6	6	11	22	9	4
(CH₂=CH)(CH₂=CH-CH₂)CHO⁻		2	2	20	44	34	100	72	17	23	32	3	6	8	12	4	4
CH₂=CH(CH₂)₂C̄HCHO		2	2	14	46	25	100	72	15	21	30	4	4	6	11	3	3

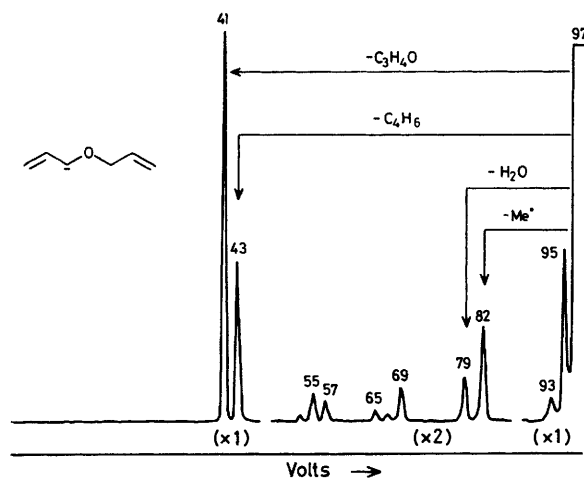| Ion	m/z	79	81	95	96
CH₂=CH-C̄HO-allyl		4	34	6	7
(CH₂=CH)(CH₂=CH-CH₂)CHO⁻		2	9	6	5
CH₂=CH(CH₂)₂C̄HCHO		2	3	4	4

Figure 1. CA mass spectrum of deprotonated diallyl ether. For experimental conditions see Experimental section. A voltage of 1 kV applied to the collision cell gives major peaks that have both collision-induced (c) and unimolecular components (u), viz. m/z (c:u): 95 (20:80), 43 (40:60), and 41 (30:70). The voltages at half height for the major peaks are [m/z (V ± 0.3)]: 95 (60.0), 82 (49.5), 79 (44.6), 43 (49.5), and 41 (34.0)
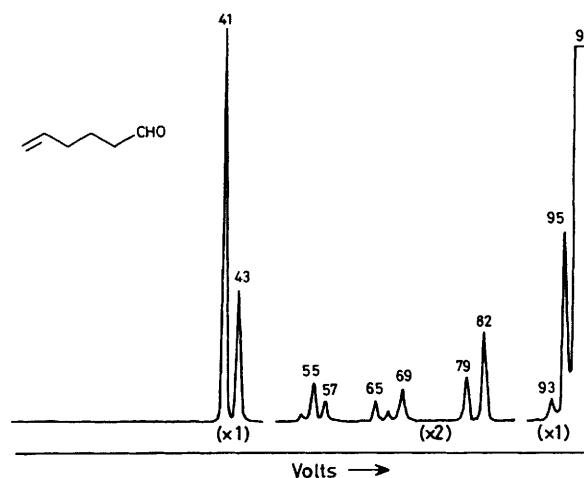
Figure 2. CA mass spectrum of CH₂=CH-(CH₂)₂-C̄H-CHO. For experimental conditions see Experimental section. A voltage of 1 kV applied to the collision cell gives major peaks that have both collision-induced (c) and unimolecular components (u), viz. m/z (c:u): 95 (15:85), 43 (50:50), and 41 (40:60). The voltages at half height for the major peaks are [m/z (V ± 0.3)]: 95 (59.6), 82 (49.1), 79 (44.5), 43 (49.0), and 41 (34.3)
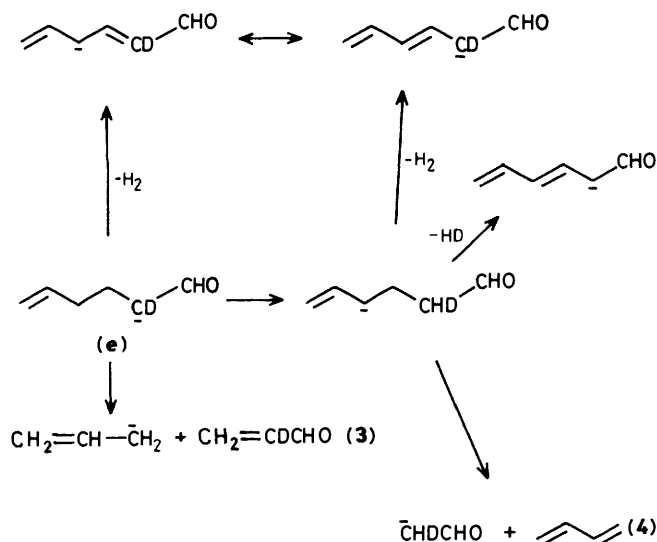
The spectral data (Table 1) of the $(M - D^+)^-$ ion (e) of [5,5-²H₂]hex-5-en-1-al best illustrates the fragmentations of (d).* Losses of H₂ and HD are likely to occur by the characteristic[15] eliminations shown in Scheme 2; other major product ions are formed as indicated in equations (3)† and (4). The proton-

transfer reaction shown in equation (4) is not unusual; similar reactions have been observed for a number of enolate negative ions.[16]

The next question to be resolved is whether the Wittig rearrangement of (a) is a normal 1,2-rearrangement (like that shown in Scheme 1) or a 1,4-rearrangement in which the carbanion attacks the terminal position of the adjacent allyl substituent. Both rearrangements occur in the condensed phase with methyl substituted allyl ethers;[3] the relative proportion of products is vitally dependent upon reaction conditions. The questions posed above may be resolved by consideration of the

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* Reaction of CH₂=CH-(CH₂)₂-CD₂-CHO with DO⁻ yields $(M - D^+)^-$: $(M - H^+)^-$ = 97:3.

† We cannot exclude the possibility that some proportion of the ions CH₂=CH-CH₂⁻ shown in Figure 1 is formed from (a) and/or (c).

Scheme 2.

CA mass spectrum of $CH_2=CH-\bar{C}DOCD_2CH=CH_2$ (see Table 1). Examination of Scheme 3 illustrates the two possible pathways. The 1,2-migration (route **A**) leads to product ions at m/z 43 and 44, whereas the 1,4-migration (route **B**) should give products m/z 43 and 45. The ratio of m/z 44 to 45 should give an indication of the relative importance of the respective 1,2- and 1,4-processes. The spectrum (Table 1) shows m/z 44:45 = 10:7, thus both 1,2- and 1,4-Wittig rearrangements occur in this system. We cannot be sure of the exact ratio of rearrangement channels, since it is probable that a deuterium isotope effect operates against the formation of m/z 45 (see Scheme 3 for the
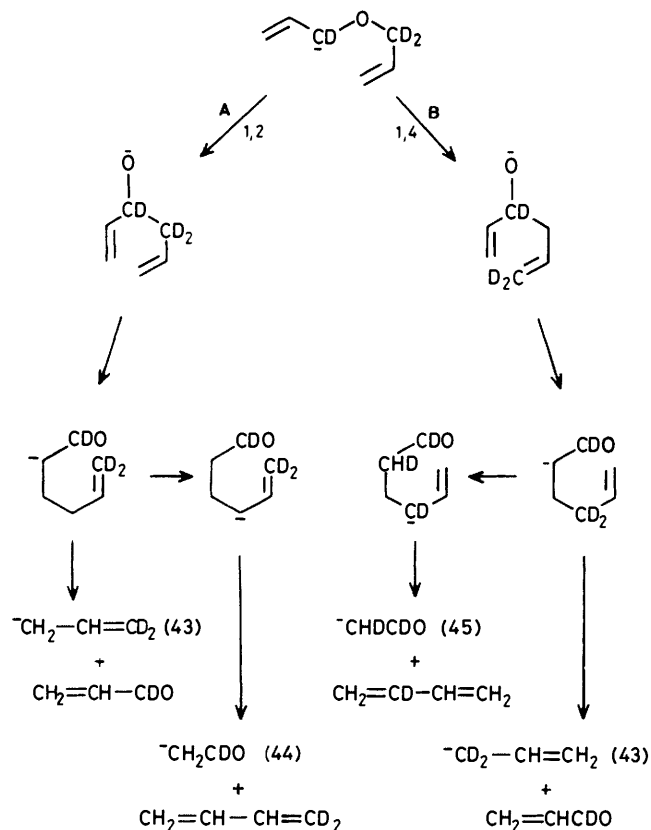
Scheme 3.

D^+-transfer process). If this is the case, a $^1H/^2H$ value of 1.45 would be sufficient to give a 1,2- to 1,4-reaction ratio of 1:1.

The final problem to be resolved is whether proton transfer can effect the conversion of (**a**) ⟶ (**b**) and whether such a conversion competes with the rearrangement (**a**) ⟶ (**c**) ⟶ (**d**). To address this problem, we have studied the CA mass spectra of ions $CH_2=CHCHOCD_2CH=CH_2$ and $CH_2=CH-CD-OCH_2CH=CH_2$, formed in the ratio 6:4 by the reaction of HO^- with $CH_2=CHCD_2OCH_2CH=CH_2$ (see Table 1). The two spectra give qualitatively similar results, but that of the D_1 ion is easier to interpret. Rearrangement and fragmentation of (**f**) (as in Scheme 3) will give product ions at m/z 41 and 44 as seen in Scheme 4. If (**f**) undergoes proton transfer to (**g**), then additional peaks will be seen at m/z 42 and 43. The spectrum of (**f**) shows $C_3H_5^-$ (m/z 41) and $C_3H_4D^-$ (42) in the ratio 100:9, with $[^-CH_2CDO/^-CHDCHO]$ (m/z 44) and $^-CH_2CHO$ (43) in the ratio 100:6 (Table 1). Thus proton transfer (**f**) ⟶ (**g**) is a minor process; greater than 90% of product ions are formed directly through (**f**).
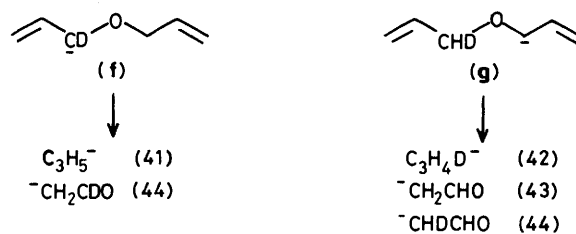
Scheme 4.

In conclusion, the answers to the questions posed in the introduction are: (i) the proton-transfer reaction (**a**) to (**b**) does not compete effectively with other rearrangements of (**a**), (ii) deprotonated diallyl ether undergoes facile 1,2- and 1,4-rearrangement reactions, (iii) the Wittig ions rearrange further by an oxy Cope mechanism.

Experimental

CA mass spectra and charge-reversal mass spectra[14] were recorded on a Vacuum Generators ZAB-2HF mass spectrometer operating in the negative chemical ionisation mode. All slits were fully open to obtain maximum sensitivity and to minimise energy-resolution effects.[17] The chemical ionisation slit was used in the ion source: ionising energy 70 eV (tungsten filament), trap current 100 μA, ion source temperature 150 °C, accelerating voltage 8 kV. Neutral species were introduced through the septum inlet at 25 °C. Carbanions were generated by H abstraction by HO^- (or H^- or O^-) or D abstraction as appropriate by DO^- or O^-). Reactant negative ions were generated from either H_2O or D_2O by 70 eV electrons.[18] The indicated source gauge pressure (of H_2O or D_2O) was typically 5×10^{-6} Torr. The substrate pressure was typically 5×10^{-7} Torr. The estimated total pressure within the source is 2×10^{-2} Torr. The pressure of He in the second collision cell was 2×10^{-7} Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of *ca.* 10% and thus corresponds to essentially single-collision conditions.

Diallyl ether was a commercial product. The following compounds were prepared by reported procedures; hexa-1,5-dien-3-ol[19] and hex-5-en-1-al.[20]

The Labelled Compounds.—$[2,2-^2H_2]Hex$-5-en-1-al. Exchange of the acidic protons of hex-5-en-1-al was effected by a

reported procedure.[21] Four exchanges with pyridine/D_2O gave the incorporation $[^2H_1]$ = 3, $[^2H_2]$ = 97%.

The $[^2H_2]$ and $[^2H_4]$diallyl ethers were prepared respectively from allyl alcohol and $[1,1\text{-}^2H_2]$allyl bromide[22] and $[1,1\text{-}^2H_2]$allyl alcohol[23] and $[1,1\text{-}^2H_2]$allyl bromide by the method used previously for benzylalkyl ethers.[9] $[^2H_2]$ and $[^2H_4]$ > 99%. The position of deuterium incorporation was shown by ^1H n.m.r. (on a Bruker 90 instrument): allylOCD$_2$CH=CH$_2$ δ 4.96—5.34 (4 H, m), 5.68—6.15 (2 H, m), and 4.00 (2 H, J 5 Hz); (CH$_2$=CHCD$_2$)$_2$O δ 4.96—5.34 (4 H, m) and 5.68—6.15 (2 H, m). No signal was observed at δ 4.00.

Acknowledgements

References

1 G. Wittig, *Angew. Chem.*, 1954, **66**, 10.
2 H. E. Zimmerman in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, London, 1963, vol. 1, 345.
3 J. E. Baldwin, J. de Bernardis, and J. E. Patrick, *Tetrahedron Lett.*, 1970, 353.
4 C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, 1951, **73**, 1437.
5 J. Cast, T. S. Stevens, and J. Holmes, *J. Chem. Soc.*, 1960, 3521.
6 P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, 1966, **88**, 78.
7 H. Schäfer, U. Schöllkopf, and D. Walter, *Tetrahedron Lett.*, 1968, 2809.
8 U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 763.
9 P. C. H. Eichinger, J. H. Bowie, and T. Blumenthal, *J. Org. Chem.*, 1986, **51**, 5078.
10 J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, 1964, **86**, 5017, 5019.
11 A. Viola and L. A. Levasseur, *J. Am. Chem. Soc.*, 1965, **87**, 1150.
12 R. P. Lutz, *Chem. Rev.*, 1984, **84**, 205.
13 M. D. Rozeboom, J. P. Kiplinger, and J. E. Bartmess, *J. Am. Chem. Soc.*, 1984, **106**, 1025.
14 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; I. Howe, J. H. Bowie, J. E. Szulejko, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **34**, 99.
15 M. B. Stringer, J. H. Bowie, and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
16 M. B. Stringer, J. H. Bowie, P. G. H. Eichinger, and G. J. Currie, *J. Chem. Soc., Perkin Trans. 2*, 1987, 385; R. N. Hayes, J. H. Bowie, and J. C. Sheldon, *Int. J. Mass Spectrom. Ion Proc.*, in press; P. C. H. Eichinger and J. H. Bowie, *Org. Mass Spectrom.*, in press.
17 P. C. Burgers, J. L. Holmes, J. E. Szulejko, A. A. Mommers, and J. K. Terlouw, *Org. Mass Spectrom.*, 1983, **18**, 254.
18 J. H. J. Dawson, Th. A. M. Kaandorp, and N. M. M. Nibbering, *Org. Mass Spectrom.*, 1977, **11**, 330; A. L. C. Smit and F. H. Field, *J. Am. Chem. Soc.*, 1977, **99**, 6471; M. B. Stringer, D. J. Underwood, J. H. Bowie, J. L. Holmes, A. A. Mommers, and J. E. Szulejko, *Can. J. Chem.*, 1986, **64**, 764.
19 L. W. Butz, E. W. Butz, and A. M. Gaddis, *J. Org. Chem.*, 1940, **5**, 171.
20 R. Ratcliffe and R. Rodehurst, *J. Org. Chem.*, 1970, **35**, 4000; M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, 1953, **18**, 1225.
21 J. E. Baldwin and R. G. Pudussery, *Chem. Commun.*, 1968, 408.
22 J. Hooz and S. S. H. Giliani, *Can. J. Chem.*, 1968, **46**, 86.
23 P. D. Bartlett and F. A. Tate, *J. Am. Chem. Soc.*, 1953, **75**, 91.