Unsaturated Carbenes from Primary Vinyl Trifluoromethanesulphonates.[1] α- *vs.* β-Elimination from Monoalkyl Primary Vinyl Trifluoromethanesulphonates

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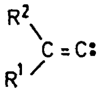
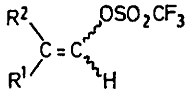
Summary Deuterium labelling studies show that elimination and acetylene formation from $R(H)C{=}CHOSO_2CF_3$ proceed *via* α-elimination by way of an unsaturated carbene, rather than an $E2$ β-elimination.

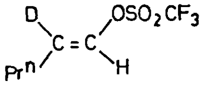
Recently we reported the generation and chemistry of unsaturated carbenes of type (**1**) from primary vinyl trifluoromethanesulphonates (**2**) and Bu^tOK.[2] Methylene cyclopropanes were obtained with a variety of olefins where $R^1 = R^2 =$ alkyl. However, only alkynes were obtained for $R^1 = R^2 =$ Ph, $R^1 =$ Me and $R^2 =$ Ph, and $R^1 = Pr^n$ and $R^2 =$ H. The alkyne $RC{\equiv}CH$ could be formed *via* two different mechanisms as shown in the Scheme: (a) $E2$ elimination of the β-proton from (**2**) or (b) α-elimination, formation of the unsaturated carbene (**1**), and hydrogen migration. In order to differentiate between these two possible mechanisms the β-deuteriated compound (**3**) was prepared from $Me[CH_2]_2CD_2CHO$ by the previously reported procedure.[2] The deuterioaldehyde was obtained by exchange of the enolizable hydrogens of methyl valerate with MeOD[3] and NaOD followed by reduction with $LiAlH_4$ and oxidation with CrO_3–pyridine.[4]



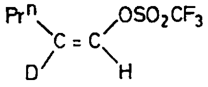
(1)



(2)

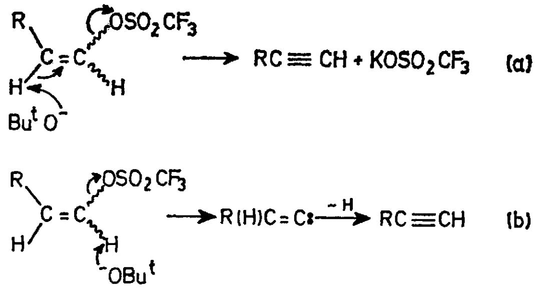


E-(3)



Z-(3)

Reactions were carried out in duplicate in cyclohexene as solvent with Bu^tOK as base at −20 °C,[2] conditions that clearly exclude a vinyl cation mechanism.[5] Partial reaction (30 and 90%) of a 48 : 52 mixture of *E*- and *Z*-(**3**) isomers and g.l.c. analysis of the reaction mixture showed that the ratio of unchanged trifluoromethanesulphonates was identical to the starting ratio, indicating a complete lack of stereochemical effects upon the elimination step, which is clearly more consistent with mechanism (b) than (a). This complete lack of stereochemical effect is in contrast to the behaviour of the *cis*- and *trans*-isomers of styryl chlorides where a preference for elimination was observed in reaction with Bu^{n}Li in ether.[6] Further evidence for mechanism (b) is provided by the absence of a kinetic deuterium isotope effect, k_H/k_D, in the reaction of either the *E* or the *Z*-isomer of (**3**). Reaction of a mixture of pure *E*-(**3**) consisting of 50·7 ± 0·2% deuteriated and 49·3 ± 0·2% non-deuteriated compounds after 83% reaction showed the recovered trifluoromethanesulphonate to contain 50·9 ± 0·8% ^{2}H and 49·1 ± 0·8% ^{1}H, which is identical, within experimental error, to the proportions in the starting material. Similarly for the pure *Z*-(**3**) isomer, the deuterium content, as determined by mass spectrometry and n.m.r. spectroscopy, of the starting and recovered vinyl trifluoromethanesulphonate after 81% reaction was identical within experimental error (39·9 ± 1·4% ^{2}H and 60·1 ± 1·4% ^{2}H). A considerable isotope effect, k_H/k_D = 2—10 would have been expected for a β-elimination.[7]



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Finally, although some (20—40%) deuterium was observed in the 1-position of the product pentyne this evidence by itself does not allow a distinction between mechanisms (a) and (b) as control experiments demonstrated that the acetylenic proton is readily exchanged with solvent (the Bu^{t}OH formed) under any reaction conditions employed.

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[1] For the previous paper in the series, see P. J. Stang and M. G. Mangum, *J. Amer. Chem. Soc.*, in the press.

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