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Evidence for concerted processes in the course of the homoallenylic transposition

Chahinez Aouf, Nicolas Galy, Maurice Santelli *

Université d'Aix-Marseille & CNRS, Institut de Chimie Radicalaire, UMR 7273, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

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Dedicated to the memory of Professor A. Guillemonat (1909–1999) who introduced allene chemistry at the University of Marseille

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Nonclassical ions
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Cyclobutanes
Tosylate hydrolysis
van der Waals interactions

ABSTRACT

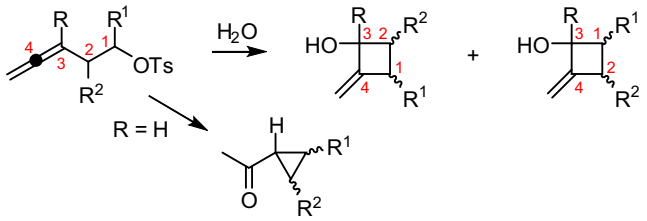
The hydrolysis of β-allenic tosylates produces mainly 2-methylenecyclobutanols resulting from a homoallenylic participation along with isomeric 2-methylenecyclobutanol minor products coming from a 1234–1243 rearrangement. Structures of various cyclopropylvinyl carbocations involved in the course of the hydrolysis have been determined by computational studies.
For acyclic tosylates, the hydrolysis of one β-deuterated allenic tosylate confirmed the nucleophilic attack on the corresponding nonclassical carbonium ion before its evolution to a *more stable* cyclopropylvinyl carbocation. In the case of one cyclic β-allenic tosylate, the structure of the products has been checked by the use of deuterated isotopomer.

1. Introduction

The interconversion reactions of cyclobutyl, cyclopropylcarbinyl and allylcarbinyl derivatives[1] began to gain increasing importance, especially after the precursor studies of P. Bruylants in 1928,[2] which dealt with the cyclisation of homoallylic chloride to give cyclopropylcarbinol and the conversion of cyclobutylamine into cyclopropylcarbinol as described by N. J. Demjanow in the early 1907[3] (Demjanow rearrangement).[4] This ionic path constitutes a major synthetic route to cyclopropane and sometimes cyclobutane derivatives in organic chemistry[5] and in biology.[6] In fact, cyclopropane derivatives are immensely favoured over cyclobutane derivatives according to the theory of ring-closing kinetics.[7]

Since 1964,[8,9] evidence from stereochemistry[10] and reaction kinetics[11] suggested the existence of an important interaction between a carbenium ion centre and a β-allenyl group in the course of the hydrolysis and acetolysis of β-allenic tosylates.[12–14] Similar results have been observed during the solvolysis of β-allenic tosylates[15] and from the nitrous deamination of β-allenic amines.[16]

Interestingly, when the β-allenyl linkage is substituted by an alkyl group (R≠H), the solvolysis reactions produce mainly the cyclobutyl derivatives along by minor products, resulting from 1234 to 1243 rearrangement.[12c] In contrast, when R=H, the homoallenylic participation affords cyclopropylketones (Scheme 1).



Scheme 1. Hydrolysis of β-allenic tosylates (co-solvent: acetone or dioxane).

This topic appears as a part of the problem of the formation of nonclassical carbocations[17,18] in the course of the polyolefin cyclisations,[19] and particularly, the fascinating problem of the biosynthesis of terpenes[20] and steroids.[21]

Our purpose is to report on the structure of carbocationic intermediates which are involved in the hydrolysis of some particular β-allenic tosylates.

For example, the two tosylates **1b** and **2b** afforded the same products, in different proportions, through hydrolysis or acetolysis (Table 1).[8,12c] As previously demonstrated, the reaction occurred with inversion of configuration at the functional carbon atom.[10,12d]

* Corresponding author. E-mail address: m.santelli@univ-amu.fr (M. Santelli).

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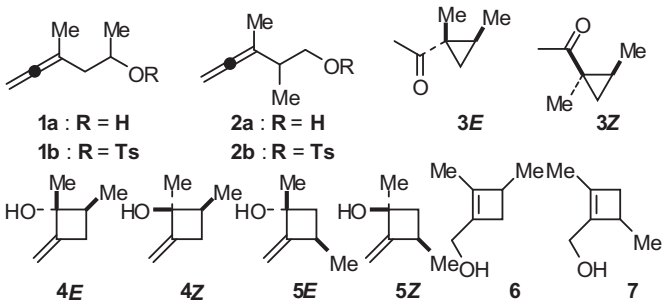
Table 1
Distribution products of the solvolysis of tosylates **1b** and **2b**



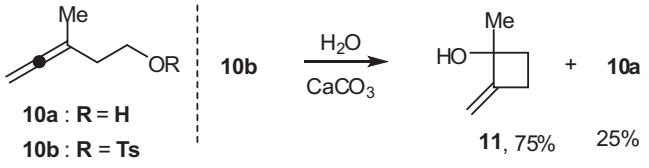
Tosylate, reaction	**1a**	3*Z*	4*E*	4*Z*	5*E*	5*Z*	**6**	**7**	[Products]/[rearr-products]
Hydrolysis:[a] **1b**	8.2	4	13.5	16	33	15	4	6.3	Σ**5**+**7**/Σ**4**+**6**=1.62
Acetolysis:[b] **1b**	7.5	0	12.4	8.1	24.5	14.4	14	19	Σ**5**+**7**/Σ**4**+**6**=1.68
Hydrolysis:[a] **2b**	2.6	9.6	25.5	33.7	13.4	7.4	6.2	1.5	Σ**4**+**6**/Σ**5**+**7**=2.93
Acetolysis:[b] **2b**	2.4	0	22.2	14.5	14.5	7.7	29	9.6	Σ**4**+**6**/Σ**5**+**7**=2.10

[a] Water–acetone, v/v=90:10, $CaCO_3$ $c=5.10^{-3}$ $t=55$ °C.
[b] Acetic acid and sodium acetate, (t=80 °C) followed by treatment with $LiAlH_4$.

Up to one third of the products possess a rearranged skeleton (**4** and **6** from **1b**[5] and **7** from **2b**).

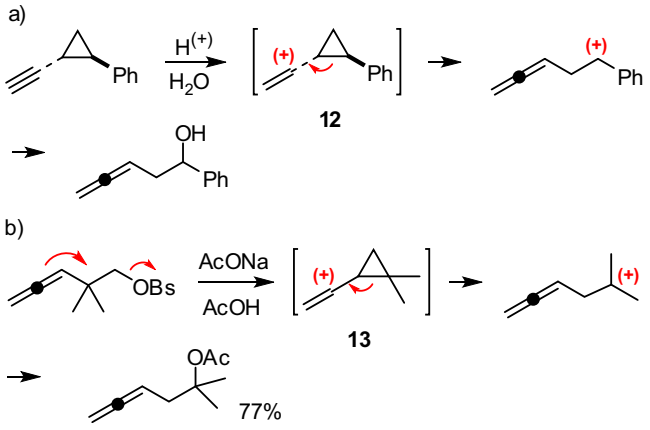
Two possible mechanisms have been postulated to rationalise the inversion of configuration at the functional carbon atom[10,12d] and the apparent exchange of the positions of the substituents: the formation of 1-cyclopropylvinyl cations,[22] or/and the formation of nonclassical carbocations with a bridged structure. These hypotheses are illustrated in Scheme 2a. Indeed, one conformation of tosylate **1b** led to methylenecyclobutanols **5***E* and **4***E* (rearranged) through 1-cyclopropylvinyl cation **8***E* or/and nonclassical carbocation **9***E*. A similar route from another conformation of **1b** gave methylenecyclobutanols **5***Z* and **4***Z* (rearranged) from 1-cyclopropylvinyl cation **8***Z* or corresponding nonclassical ion (Scheme 2b). These cycle enlargements are induced by the neopentylic structure of carbocations **8***E* and **8***Z*.

Hydrolysis of primary tosylate **10b** mainly afforded methylenecyclobutanol **11** and, as a result, the reaction has preparative importance (Scheme 3).

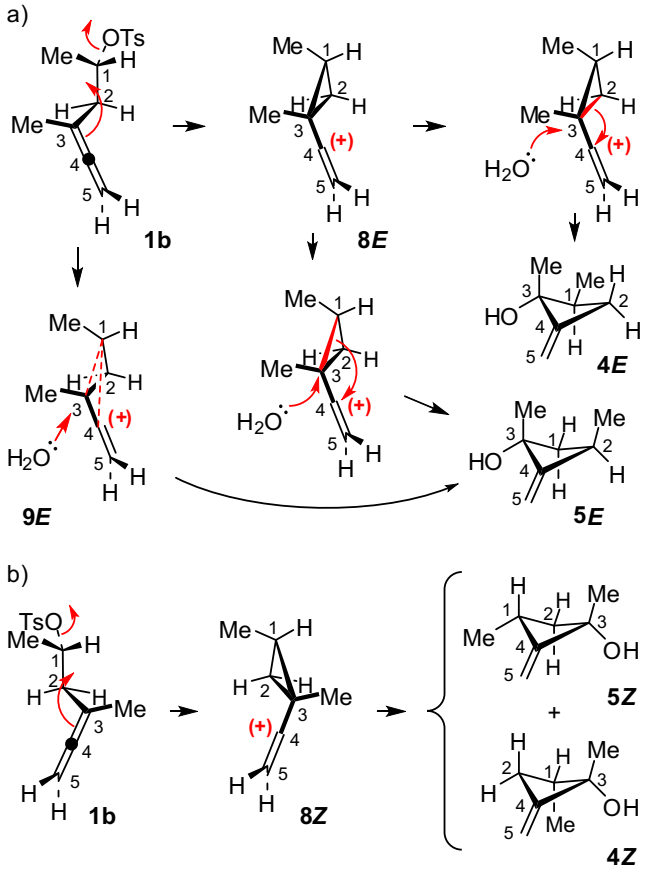


Scheme 3. Hydrolysis of the tosylate **10b** (water–dioxane, 75:25).

The ring-opening of 1-cyclopropylvinyl cations to the corresponding homoallenyl derivatives and the reverse reaction are well-known. Recently, Baines and co-workers have demonstrated that an α-cyclopropylvinyl cation **12** generated by protonation of *trans*-1-ethynyl-2-phenylcyclopropane underwent a selective ring-opening towards the phenyl substituent leading to the β-allenic alcohol (Scheme 4a).[23,24] Clearly, the benzyl cation is more stable than the cyclopropylvinyl cation **12**.



Scheme 4. Ring-opening of 1-cyclopropylvinyl cations **12** and **13**.



Scheme 2. Solvolysis pathways of the tosylate **1b**.

In 1967, Bly and Koock observed that the acetolysis of neopentylic β-allenic brosylates occurred without formation of cyclised products but with enhanced rates compared to the corresponding saturated brosylates (Scheme 4b).[25] Their hypothesis that the 1-(2,2-dimethylcyclopropyl)vinyl cation **13** was unstable with respect to the acyclic tertiary β-allenyl cation is in accordance with the Baines' experiments.

2. Results and discussion

All calculations were performed with the *Gaussian 09*, revision A02, suites of program.[26] Structures of the carbocationic intermediates were calculated at the B3LYP,[27] B3PW91[28] and MP2[29] levels using the 6-311G++(d,p), or 6-311G++(3df,3pd) basis sets. A vibrational analysis was performed at the same level of theory in order to determine the zero-point vibrational energy (ZPE) and to characterise each stationary point as a minimum (Nimag=0). The total energies, ΔE were evaluated at 0 K and the Gibbs free energy ΔG, at 298.15 K. All calculations were performed using water as solvent (Polarisable Continuum Model) (calculated geometries by using ideal gas are given in the Supplementary data, Tables 1–4). The stabilisation of carbocations induced by the presence of water is from 47 to 52 kcal/mol. Structures calculated in water are more compact than those calculated in ideal gas (see, Supplementary data, pages 7–9).

2.1. Solvolysis of acyclic β-allenic tosylates

The calculated geometries, employing various levels of theory, have shown that the parent 1-cyclopropylvinyl cation **14** resembled to the bisected cyclopropylcarbinyl cation with a large C1–C3 (or C2–C3) bond length and a short C1–C2 one (Fig. 1a and in Supplementary data, Table 1).[30]

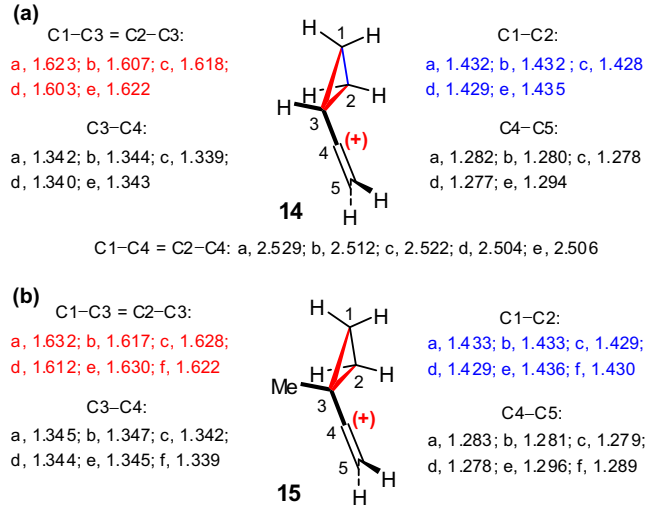
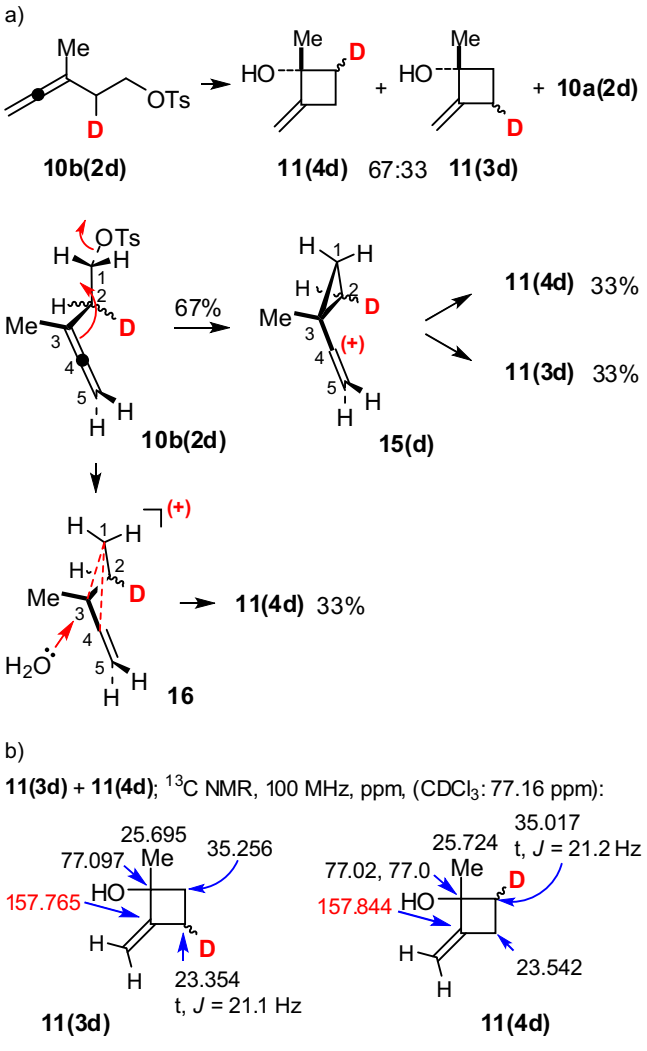


Fig. 1. Bond lengths and angles of the optimised structures of 1-cyclopropylvinyl cations **14**, and **15** calculated according to the levels of theory a–f (bond lengths are in angstroms) (longest bonds are in red, and shortest bonds in blue) (solvent: water).

Concerning the solvolysis of **10b**, the structure of the corresponding carbocationic intermediate **15** is very similar to that of **14**, the major difference is the shorter C1–C4 bond distance (Fig. 1b and in Supplementary data, Table 1). Interestingly, for a bridged nonclassical ion, one would expect that the C3–C4–C5 angles to deviate significantly from 180°. In fact, in the various structures, values are higher than 178°.

Therefore, the calculated cyclopropylvinyl cation **15** has a bisected form and consequently, the Wagner–Meerwein rearrangement leading to cyclobutanol **11** will involve the two bonds C1–C3 and C2–C3 with equal facility. To check this statement, the labelled tosylate **10b**(**2d**) has been hydrolysed (80 °C, water–acetonitrile, 90–10% v/v) and the deuterium distribution in the cyclobutanol **11**(**d**) (75% yield) determined by NMR spectrum analysis of the (*Z*)-methylenic proton coupling constant[12e] and the ^{13}C NMR of the C(2) carbon atom (Scheme 5b, and in Supplementary data, Figs. 1–4). From cation **15**(**d**) and because of symmetry (neglecting a possible very minor isotope effect), there is an equal probability of forming the two rearranged products **11**(**4d**) and **11**(**3d**) (Scheme 5a). The 33% 'excess' of unrearranged methylenecyclobutanol **11**(**4d**) suggests that the cyclopropylvinyl cation **15**(**d**) is not the sole product-forming ion and that an alternate pathway exists.



Scheme 5. Hydrolysis of the labelled tosylate **10b**(**2d**).

An explanation is the rapid solvent capture of the carbonium ion **16** before its complete isomerisation into more stable cyclopropylvinyl cation **15**(**d**). Thus, the transition state under solvolytic conditions can involve an unstable carbocation because, according to Winstein, 'there are good reasons to expect carbon bridging lags behind C–X elongation at the transition state'.[31]

Previous results have confirmed this statement. Hydrolysis of the silylated tosylate **17b** led mainly to the trimethylsilylethynylcyclopropane **18**.[32] In this case, the vinyl cation **20**, stabilised by the β-trimethylsilyl substituent,[33] (Fig. 2), release a proton before its capture by the solvent. The cyclobutanol **11** could result from the nucleophilic attack to the bridge cation **19** (Scheme 6).

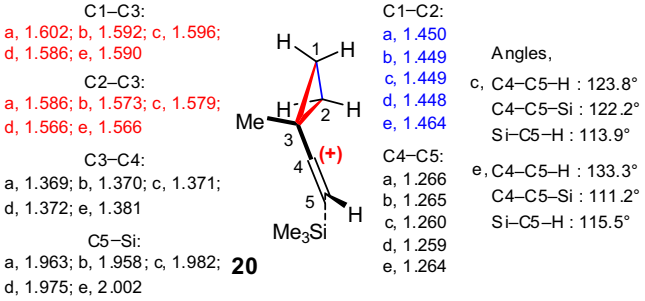
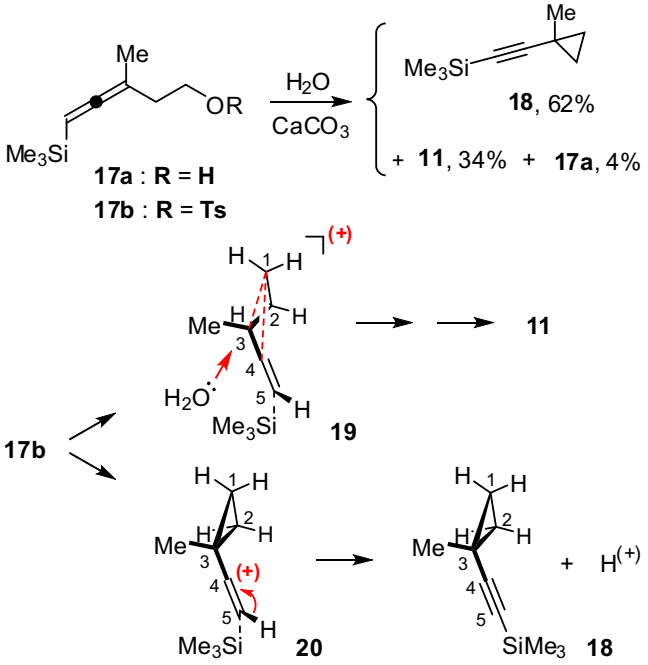


Fig. 2. Bond lengths and angles of the optimised structures of 1-cyclopropylvinyl cation **20** calculated according to the levels of theory a–e (bond lengths are in angstroms) (longest bonds are in red, and shortest bonds in blue) (solvent: water).



Scheme 6. Hydrolysis of the trimethylsilyl substituted tosylate **17b**.

Fig. 3 shows the optimised geometry of the dimethylcyclopropylvinyl cations **8***E* and **8***Z*. The added methyl group induced a dissymmetrisation of the cyclopropyl subunit with an elongation of the C1–C3 bond in comparison to the cyclopropylvinyl cation **15**. The calculated structure **8***E*, corresponds to a compromise between the classical 1-cyclopropylvinyl cation **8***E*, and the bridged structure **9***E*.

The less stable *Z*-isomer **8***Z* (**8***E*/**8***Z*, $\delta\Delta G \sim 0.32$ kcal/mol, see in Supplementary data, Table 2) is perturbed by nonbonded interactions between the methyl and vinyl groups which induced an

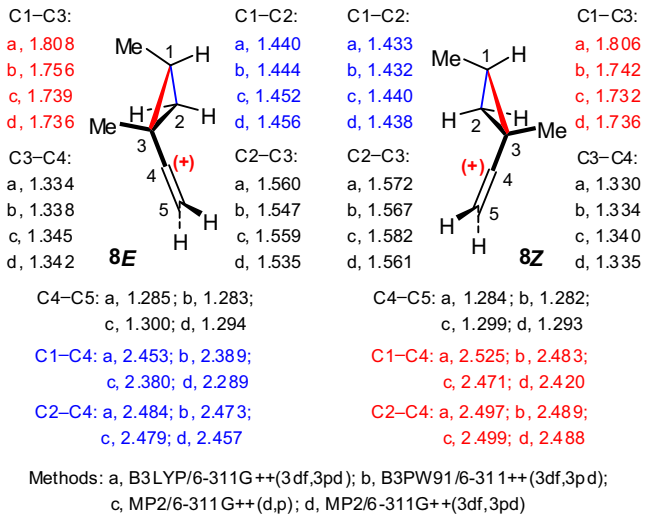


Fig. 3. Bond lengths of the optimised structures of 1-cyclopropylvinyl cations **8***E*, and **8***Z* calculated according to the levels of theory a–d (bond lengths are in angstroms) (longest bonds are in red, and shortest bonds in blue) (solvent: water).

increasing of the C1–C4 distance (and also the C1–C3–C4 angle, B3LYP/6-311G++(3df,3pd): **8***E*, 101.6; **8***Z*, 106.2; MP2/6-311G++(3df,3pd): **8***E*, 100.2; **8***Z*, 106.4°). These differences of structure can explain the greater formation of methylenecyclobutanols *E* (**4***E***5***E*) with respect to *Z* ones (**4***Z***5***Z*).

Concerning the optimised structures **8**, the double bond character of the C1–C2 bond can be represented by considering this 1-cyclopropylvinyl cation as a π-complex of an allenyl cation and an alkene (for similar considerations in cyclopropylcarbinyl cations, see Ref. 34)(Fig. 4a). The relative sizes of component atomic orbitals of the LUMO are considered in Fig 4c. Clearly, the most electrophilic carbon atoms are C1 and C4 (Fig. 4b).

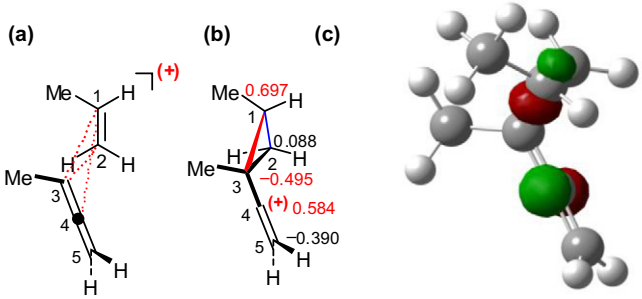
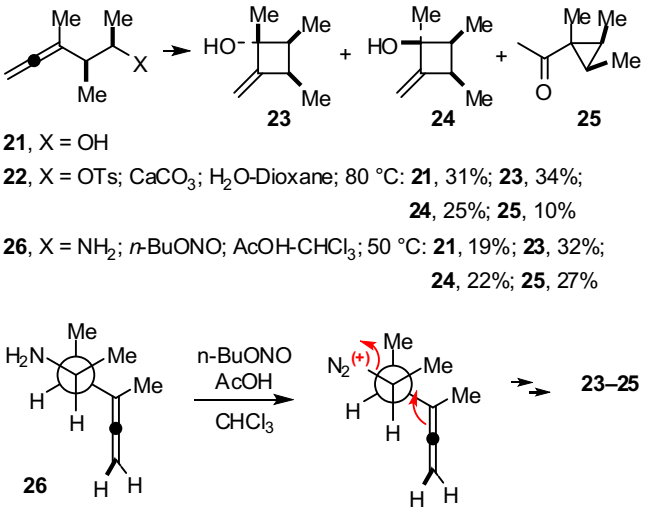


Fig. 4. (a), Structure, (b), atom polarisability tensor-based charges and (c), LUMO (27th MO) of the cyclopropylvinyl cation **8***E* (B3LYP/6-311G++(3df,3pd) level of theory, solvent: water).

The trend of the calculated structures using the B3LYP/6-311G++(3df,3pd) is similar to MP2/6-311G++(3df,3pd) level of theory. According to previous works, it appears that MP2 often tends to overestimate the stability of 'nonclassical' structures (MP2 is generally more appropriate than DFT for describing noncovalent interactions that are more dependent on dispersion interactions).[35] In fact, MP2 calculations predicted a stronger bridging in **8** than B3LYP calculations, as evidenced by the smaller crucial bond lengths C1–C3, C1–C4 and C2–C4 (Fig. 3).

Concerning the nitrous deamination[36] of β-allenic amines performed in protic and aprotic media, on seven cases studies, only one, the *threo* amine **26**, gave rise to a homoallenyl participation (in aprotic media) and even with a better yield of 81% than the

hydrolysis of the corresponding tosylate **22** (69%) (Scheme 7).[16] Interestingly, in both cases, the participation occurred with inversion of configuration at the functional carbon atom.



Scheme 7. Nitrous deamination of amine *threo* **26** and hydrolysis of the corresponding tosylate **22**.

We propose that the different behaviour of β-allenic amines can be explained by the tendency of **26** to adopt a conformation in which the reactive sites are close.

Optimisation by molecular mechanics followed by calculation at the B3LYP/6-311G++(d,p) level of theory, shown that for the amine **26**, in the more stable conformation (ΔE=−368.684416 au) (Scheme 7), the allenyl moiety was in the rear part of the functional carbon atom allowing a rearward attack on diazonium ion with minor conformational changes. The participation should be made easier according to the principle of least motion,[37] which states that those elementary reactions will be favoured, involving the least change in atomic position and electronic configuration.

2.2. Solvolysis of cyclic β-allenic tosylates

Then, we investigated the case of tosylates **27b** and **28b** the solvolysis of which gave complicated product mixtures (Fig. 5).[12g]

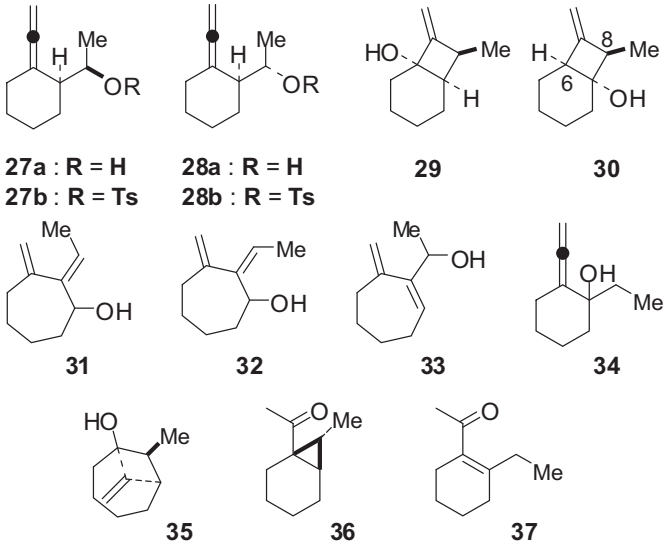


Fig. 5. Hydrolysis products from tosylates **27b** and **28b**.

The structure of the unexpected cyclobutanol **30** was established on the basis of two dimensional NMR spectra (HMQC and NOESY).

Instead of solvolysis in 25% dioxane–water mixture used previously, we chose acetonitrile–water mixtures which appeared to be ones of the less complicated aqueous binary mixtures. Indeed, acetonitrile competes successfully with water–water interactions and destroys the lattice structure.[38] Remarkably, hydrolysis of **27b** in water–acetonitrile mixture led quantitatively to a mixture of only four alcohols, **29**, **30**, **31** and **33** (Table 2). We note the absence of **27a**, **28a** and **32**. Therefore, the participation reaction is the sole possible process. The high ionising power *Y* of the mixture water–acetonitrile 90–10 (as given by the Grunwald–Winstein equation)[39] of this mixture (*Y*=3.03, extrapolated from data for water–acetonitrile 20–80 to 80–20[38b]), also shows that the participation reactions were favoured by increasing solvent polarity.[12e,40] From **28b**, hydrolysis in water–acetonitrile mixture (90–10%, v/v) led to **28a**, 19%; **32**, 15%; **34**, 12%; **35**, 42%; **36**, 8% and **37**, 4%.

Table 2
Hydrolysis products of **27b** and **27b**(**d**) (*c*=0.03 mol/L, 80 °C)

Solvent	*Y*	**29** (%)	**30** (%)	**31** (%)	**33** (%)
H_2O–Acetonitrile 90:10% v/v	3.03	30	28	18	24
H_2O–Acetonitrile 50:50% v/v	1.50	25	26	21	28
		29(**d**)	**30**(**d**)	**31**(**d**)	**33**(**d**)
H_2O–Acetonitrile 90:10% v/v	3.03	28	34	14.5	23.5

The corresponding diastereoisomeric 1-cyclopropylvinyl cations **38** and **39** show different optimised structures (Fig. 6) (**38**/**39**, $\delta\Delta G$=3.08–3.15 kcal/mol, see in Supplementary data, Table 3). If C1–C2 bonds have similar bond lengths, nonbonded interactions induced by the presence of the methyl group strongly modified the C1–C3 and C2–C3 bond lengths. For the less stable cation **38**,

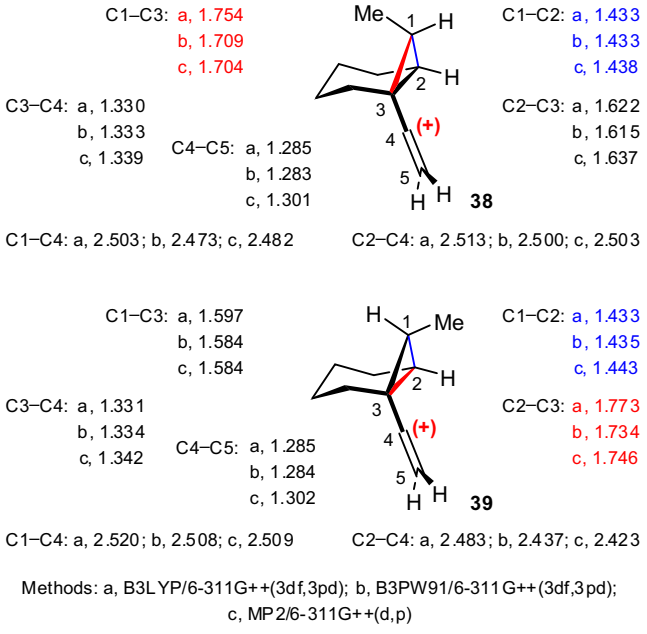
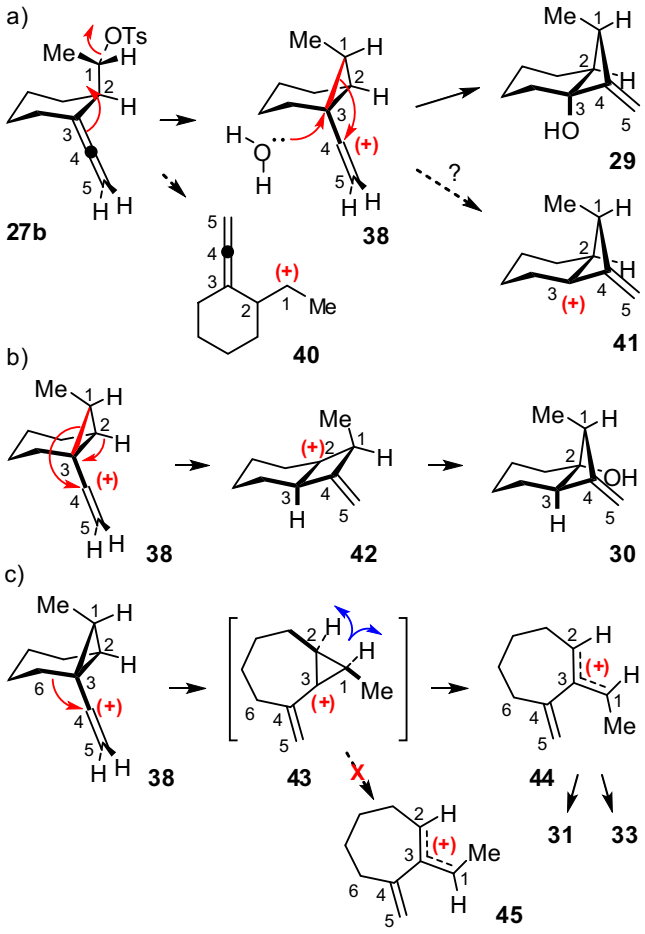


Fig. 6. Bond lengths of the optimised structures of 1-cyclopropylvinyl cations **38**, and **39** calculated according to the level of theory of calculation a–c (bond lengths are in angstroms) (longest bonds are in red, and shortest bonds in blue) (solvent: water).

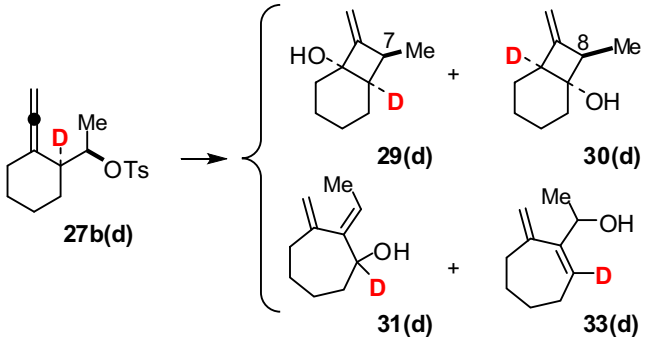
interactions between the methyl and cyclohexane groups elongated the C1–C3 bond. However, the significant C2–C3 elongation in **39** is due to the interactions between the methyl and the vinylic cation. As for the precedent cases, MP2 calculations led to stronger bridged structures. Values for atom polarisability tensor-based charges (APT charges)[41] are also different particularly for C1 (highest value for **38**) and C2 (highest value for **39**) (Supplementary data, Fig. 9).

Hydrolysis products resulting from **27b** and **28b** are different. This result is the consequence of the inversion of configuration at the functional carbon atom of these tosylates, which induces the difference of structure of the corresponding vinyl cations **38** and **39**, respectively (the free β-allenyl cation **40** is not formed). The fact that different compounds are produced strongly suggests a series of stepwise rearrangements, where each step is probably concerted. From **38**, the major product is the methylenecyclobutanol **29** arising from a Wagner–Meerwein rearrangement involving the C1–C3 bond. A concerted route joining a nucleophilic attack and the 1,2-shift can explain the diastereoselectivity and rule out the intervention of the free cyclobutyl cation **41** (Scheme 8a).[42] The formation of the second methylenecyclobutanol **30** implied the same ring enlargement followed by a 1,2-hydride ion migration ('β-hop')[43] to give the convex tertiary cation **42**. The nucleophilic attack occurred on the most accessible face (Scheme 8b).[44] We note that the formation of major products **29** and **30** resulted from the migration of the longest C1–C3 bond of the cyclopropane moiety of **38**. The most striking products **31** and **33** resulted from a Wagner–Meerwein rearrangement with migration of the C3–C6 bond (Scheme 8c). This exceptional migration seems due to relief of nonbonded interactions between the methyl and cyclohexyl groups. Then, the resulting planar cyclopropyl cation intermediate **43** opens according to a disrotatory process in a direction dictated by steric preferences to give the *Z*-methylallyl cation **44** precursor of alcohols **31** and **33**.[45,46] During the optimisation at the B3LYP/6-311G++(d,p) level, the geometry of cyclopropyl cation **43** converged to the more stable isomer **44**.



Scheme 8. Hydrolysis pathways for the tosylate **27b** (in red longest bond).

Hydrolysis of deuterated tosylate **27b**(**d**) confirmed the hydride migration in the course of the formation of **30** from **38** (Scheme 9). In the proton NMR spectra of unlabelled **30**, signals of the methylenic group at 4.76 and 4.72 ppm were triplet (^4J=2.72 Hz, coupling with H6 and H8, Fig. 5). For deuterated **30**(**d**), similar signals at 4.74 and 4.70 ppm were doublet (coupling with H8, ^4J=2.51 and 2.84 Hz, respectively). Moreover, the multiplet at 2.72 ppm (H6 and H8) for **30** became a qdd corresponding to only H8 in **30**(**d**). For the labelled alcohol **29**(**d**), the signal of the proton H7 was a quartet instead of a doubled quartet for unlabelled alcohol **29**. The signal at 4.32 ppm had disappeared for **31**(**d**) (as the signal at 74.4 ppm in the ^{13}C NMR spectra) and for **33**(**d**) the signal at 5.84 ppm was missing (as the signal at 124.6 ppm in the ^{13}C NMR spectra). The proportion of **30** was more important in the labelled products (Table 2). However, in the course of a transannular 1,5-hydride shift, no primary isotope effect has been observed when hydrogen atom known to migrate was replaced by deuterium atom.[47]



Scheme 9. Hydrolysis of labelled tosylate **27b**(**d**).

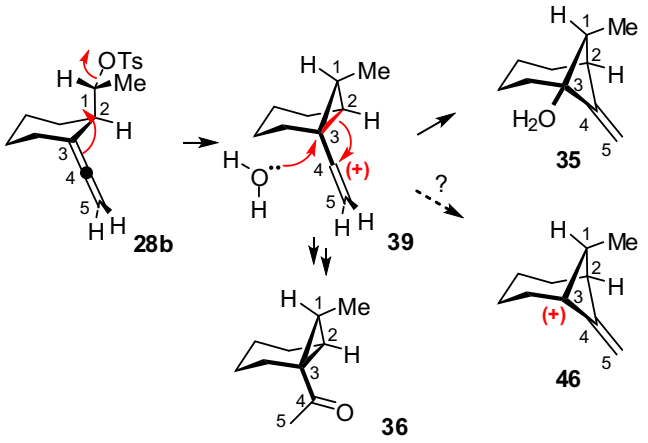
The relative stability of the vinyl cation **39**, arising from the ionisation of tosylate **28b**, with respect to **38** (Table 3) can explain that it is the sole cyclopropylvinyl cation trapped by water to give corresponding cyclopropyl ketone **36**. Calculations have shown that for **39**, the longest bond of the cyclopropane was C2–C3 (Fig. 6) and, pleasantly, the major product, **35**, arose from its migration (Scheme 10). The concerted process is evidenced by the instability of the nonplanar twisted methylenecyclobutyl cation **46**. It is likely that the discrete allylic cation **46** does not actually exist.

Table 3
Relative Gibbs free energies of various isomeric carbocations in comparison with β-allenyl cation **40**

Cation	Level of theory	δΔ*G* (kcal/mol)	Level of theory	δΔ*G* (kcal/mol)
40	a	0	b	0
38	a	−7.1	b	−12.4
39	a	−10.2	b	−15.3
41	a	−12.8	b	−15.3
42	a	−8.8	b	−19.4
44	a	−26.5	b	−26.2
45	a	−24.5	b	−22.9
46	a	−3.5	b	−13.3

Level of theory, a: B3LYP/6-311G++(3df,3pd); b: MP2/6-311G++(d,p) (solvent: water).

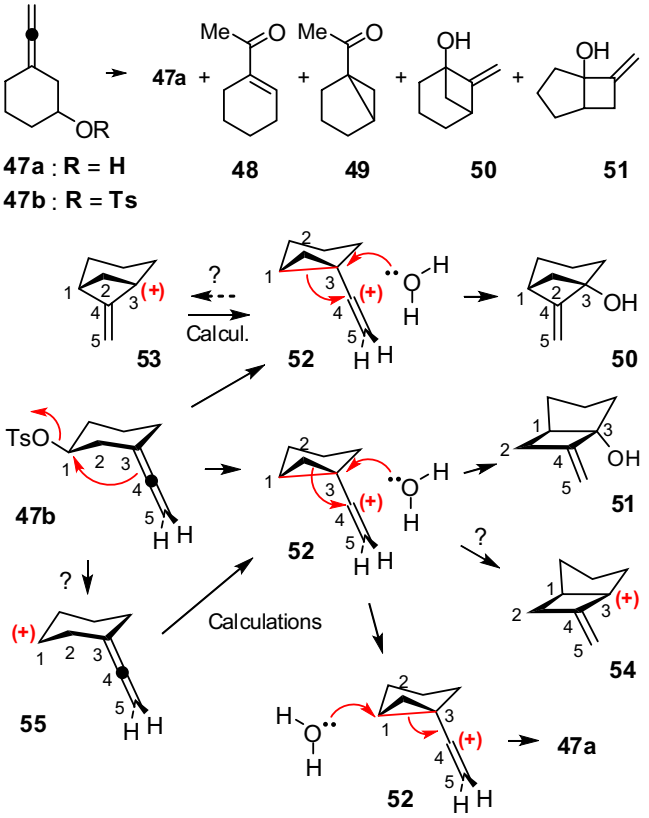
The comparative energies relative to the β-allenyl carbocation **40** and of the various cationic intermediates probably involved in the solvolysis of **27b** and **28b** are given in Table 3. We note that 1-cyclopropylvinyl cations **38** and particularly **39** are more stable



Scheme 10. Hydrolysis pathways for the tosylate **28b** (longest bond is in red).

than their corresponding opened isomer **40**. In fact, the allenyl linkage shows a high experimental standard enthalpy of formation (3-methyl-1,2-butadiene, ΔH_f°=30.88 kcal/mol; isomeric 2-methyl-1,3-butadiene, ΔH_f°=18.11 kcal/mol)[48] which explains its high chemical reactivity.

The case of tosylates of 3-vinylidenecycloalkanols and particularly **47b** is interesting because strained bicyclic cyclobutanols **50** and **51** are obtained in moderate yields (Scheme 11)(H_2O–THF 70:30, 60 °C, **47a**, 20%; **48**, 8.6%; **49**, 15%; **50**, 12.6%; **51**, 32.4%).[49]



Scheme 11. Hydrolysis pathways for the β-allenic tosylate **47b**.

Even more than previously, the formation of these compounds and particularly **50** results from concerted processes. The corresponding methylenecyclobutyl cation **53** is very strained (twisted). Our DFT studies of the cation **53** at the B3LYP/6-311++(d,p) level showed that it is not a minimum on the potential energy surface and spontaneously it rearranged into the vinyl cation **52**.

In the optimised geometry of vinyl cation **52**, the longest bond of the cyclopropane is C1–C3 (Fig. 7), and the important proportion of allenic alcohol **47a** after hydrolysis can be explained by opening of the cyclopropane to give **55** and then **47a**, or a concerted opening with the nucleophilic attack to C1 (Scheme 11). Contrary to the precedent cases, the 2-methylenecyclobutyl cation **54** is less stable than its precursor, the corresponding 1-cyclopropylvinyl cation **52**, by 1.85 kcal/mol (B3LYP/6-311++G(3df,3pd)) and 5.09 kcal/mol (MP2/6-311++G(d,p)) (Supplementary data, Table 4).

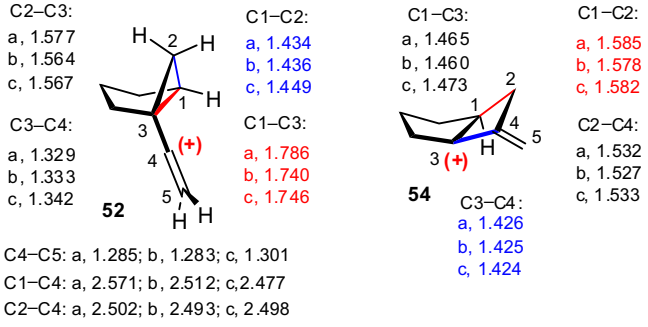


Fig. 7. Bond lengths of the optimised structures of 1-cyclopropylvinyl cations **52**, and **54**. Bond lengths are in angstroms (longest bonds are in red, and shortest bonds in blue).

3. Crystallographic study of tosylate 27b

The structure of tosylate **27b** was unambiguously confirmed by single crystal X-ray analysis (Figs. 8 and 9). A careful examination of its geometry showed that the C–O bond was almost antiperiplanar to the C3–C4 bond and that an *attractive* force brought closer the functional carbon atom and the allene linkage. The internuclear distance between the functional carbon atom and the central carbon atom of the allenyl linkage (2.830 Å) is close to the van der Waals minimum. As there are no intermolecular interactions (measured on the basis of the sum of the van der Waals radii +0.2 Å) between the allene moiety and neighbouring molecules, we can assume that this deformation (a>b, c<d) is intrinsic to our compound.

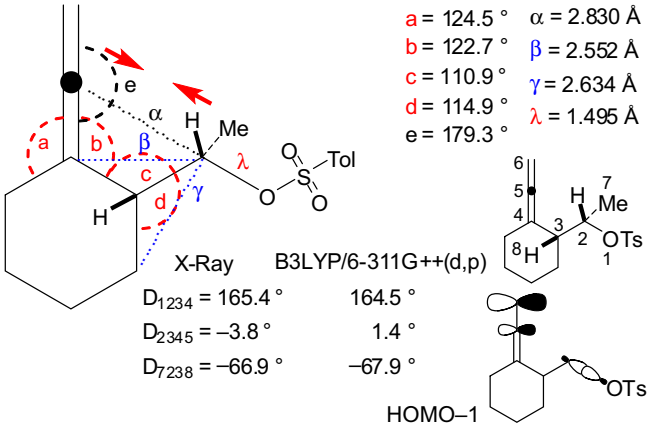


Fig. 8. Geometry of the crystallised tosylate **27b** and calculated conformation at the B3LYP/6-311G++(d,p) level of theory.

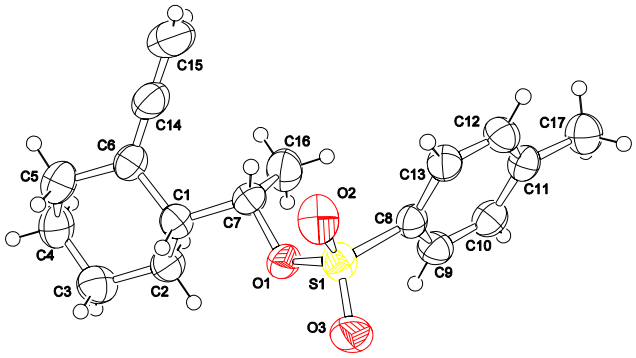


Fig. 9. ORTEP diagram of tosylate **27b**.

This stabilising interaction may include (1) attractive Coulombic interactions of bond dipoles; (2) delocalisation of valence electrons of the C–C double bonds into the LUMO orbital of the C–O bond; (3) stabilising van der Waals interactions between the two functional groups.[50] Intramolecular van der Waals attraction induced the preference for a 'crowded' *syn* conformation of 1,*n*-di-alkyl-substituted aromatic or hetero-aromatic rings.[51] More recently, the preferential formation of spiroacetals with a folded structure relative to an extended structure has been explained by the presence of van der Waals attractive interactions.[52] But, these interactions sometimes referred to hydrophobic bonding in biochemical literature,[53] result from nonbonded interactions between alkyl groups. In the case of **27b**, the attractive interaction occurred between polar functionalities and the conformation of the tosylate group is in accordance with an electron delocalisation which anticipates the homoallenylic participation. We note that the future ionised bond distance C–O (1.495 Å) is superior to the corresponding mean bond distances in some secondary 2-alkyl tosylates. A survey of the Cambridge Crystallographic Database revealed that the mean distance is 1.461±0.016 Å (n=12).

A correlation between the lengths of C–O bonds and the rates at which the same bond is broken heterolytically in solution has been proposed by Kirby: the longer the bond, the faster it breaks.[54] Calculations of the structure of **27b** at the B3LYP/6-311G++(d,p) led to the same ground-state conformation that in solid state (**27b**: ΔE=−1285.081072 au). The largest coefficients of the High Occupied MO (HOMO) are at the C4 and C5 [HOMO, 82nd MO, (E=−0.24845 au), Σatom. coef.(|2s|,|2p|): O1, 0.011; C2, 0.011; C4, 0.248; C5, 0.247; C6, 0.077] and for the HOMO-1 at the C5 and C6 [HOMO-1, 81st MO, (E=−0.26461 au), Σatom. coef.(|2s|,|2p|): O1, 0.076; C2, 0.053; C4, 0.112; C5, 0.227; C6, 0.362]. We note that an electron transfer occurred from the C5–C6 double bond towards the C–O bond.

4. Conclusions

The driving force of these solvolysis reactions is the strained energy of the allenyl linkage which afforded the cyclobutyl framework in high yields. So, methylenecyclobutanols or bicyclic methylenecyclobutanols can be obtained by this way in good yields from easily prepared β-allenic alcohols. For example, strained bicyclo[3.2.0]heptanes scaffold can be obtained from β-allenic alcohol **47a** via the hydrolysis of its tosylate ester **47b** (Fig. 10).

Calculations have shown that the main carbocationic intermediates are the 1-cyclopropylvinyl cations. But, experimental results observed from the hydrolysis of **10b**(**2d**) show that the solvent can react during the cyclopropylvinyl cation formation from the β-allenyl tosylate ionisation.

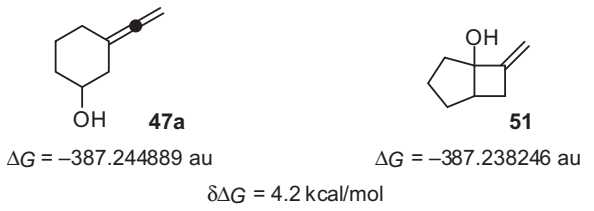


Fig. 10. Relative stability of a precursor β-allenyl alcohol and the corresponding methylenecyclobutanol product (B3LYP/6-311G++(3df,3pd) level of theory; solvent: water).

The constraint structure of some products excludes their formation through bicyclic carbocations. Results are in accordance with a concerted process with a remote nucleophilic attack by the allenic linkage followed by the ionisation step of the tosylate. Therefore, the chirality is preserved in the course of the hydrolysis.

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Supplementary data

Table 1: Calculated energies for geometry-optimised conformations of 1-cyclopropylvinyl cations **14, 15** and **20**. Table 2: Calculated energies for geometry-optimised configurations of **8***E*, and **8***Z*. Table 3: Calculated energies for geometry-optimised configurations of **38**, and **39**. Table 4: Calculated energies for geometry-optimised configurations of various carbocations involved in the solvolysis of **27b**, **28b** and **47b**. Figs. 1–4: Calculated structure of various carbocations in the ideal gas. Figs. 5–8: ^{13}C NMR of deuterated methylenecyclobutanols **11(3d)** and **11(4d)**. Fig. 9: Atom polarisability tensor-based charges of **38** and **39**. X-ray crystallographic data concerning **27b**. Experimental section: preparation of tosylates and ^{1}H and ^{13}C NMR data of (*E*)-2-ethylidene-1-ethynylcyclohexanol, 2-(1-acetoxyethyl)-1-ethynylcyclohexene, 2-(1-hydroxyethyl)-1-ethynylcyclo-hexene, **4***E*, **4***Z*, **10a**, **10a(2d)**, **10b**, **10b(2d)**, **11**, **11(3d)**, **11(4d)**, **27a**, **27b**, **27b(d)**, **28a**, **28b**, **29**, **29(d)**, **30**, **30(d)**, **31**, **31(d)**, **32**, **33**, **33(d)**, **34**, **35**, **37**, **47a**, **47b**, **49**, **50**, **51**. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2013.02.048.

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