Tetrahedron 70 (2014) 3621–3629

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An investigation of the scope of the 1,7-electrocyclization of α,β:γ,δ-conjugated azomethine ylides

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ARTICLE INFO

Article history:
Received 30 January 2014
Received in revised form 11 March 2014
Accepted 24 March 2014
Available online 12 April 2014

Keywords:
Azomethine ylides
1,5-Electrocyclization
1,7-Electrocyclization
PyrrolinesA azepines

ABSTRACT

Substituents on the diene component have little influence on the periselectivity of the cyclizations of α,β:γ,δ-conjugated azomethine ylides, with 1,7-electrocyclizations predominating. In some cases, subtle changes to these substituents can, however, influence the product formed, through their effect on the relative energies of the transition states for the 1,5- (6π) and 1,7-electrocyclization (8π) processes. The most striking changes in periselectivity occur for phenylethenyl-substituted azomethine ylides **3d**–**f**, which can give either a pyrroline **4d**,**f** or dihydrobenzazepine **6e**, depending upon the alkene configuration.

1. Introduction

Azomethine ylides, e.g., **3**, Scheme 1, can be used in the preparation of a range of heterocycles through 1,3-dipolar cycloadditions,[1] 1,5-electrocyclizations,[2] or 1,7-electrocyclizations,[3,4] and routes to these versatile intermediates include the decarboxylation of iminium salts,[5] the ring-opening of aziridines,[6] and the 1,2-prototropy of α-imino esters.[7] In continuation of our previous studies on these allyl anion type 1,3-dipoles, we describe here an investigation of the scope of the 1,7-electocyclization of α,β:γ,δ-conjugated azomethine ylides **3**. In all cases, the azomethine ylides **3** in this study were generated by the decarboxylation of an iminium salt **2** formed by the condensation of an aldehyde **1** and sarcosine (*N*-methylglycine), Scheme 1.

2. Results and discussion

Generation of the (*E*)-azomethine ylides **3a**–**c**, from the corresponding aldehydes **1a**–**c**, led to the expected formation of the pyrrolines **4a**–**c** via a 1,5-electrocyclization, Scheme 2 (pyrrole **5** was obtained as a minor product of the cyclization of azomethine ylide **3a**). Isomerization of the double bond, from (*E*)-**3c** to (*Z*)-**3c′**, and subsequent 1,7-electrocyclization onto the aryl ring, was only observed for the 4-chloro derivative **3c**, from which a minor amount of the dihydrobenzazepine **6c** was also obtained.

The 1,7-electrocyclization of the azomethine ylide **3e**, in which the configuration of the β-phenylethenyl group is (*Z*), gave the dihydrobenzazepine **6e**. Intriguingly, the azomethine ylides **3d**,**f** in which only the configuration of the β-phenylethenyl substituent has changed, to (*E*), were found to undergo 1,5-electrocyclization, giving the pyrrolines **4d**,**f** in good to excellent yield, Scheme 3.

As can be seen from Fig. 1, the (*E*)-configuration of the phenylethenyl substituent results in a greatly reduced separation between the methylene terminus of the azomethine ylide **3d** and the quaternary carbon to which it cyclizes in a 1,5-electocyclization (6π), resulting in a dramatically lower energy barrier for this process and a change in the periselectivity, to give the pyrroline product **4d** of a 1,5-electrocyclization. Molecular modelling of this process, Table 1 and Fig. 2, confirms the similar energy barriers for the 1,7-electrocyclizations of both dipoles (**3d** and **3e**), Fig. 2 (blue); the increased energy barrier for the 1,5-electrocyclization for the (*Z*)-alkenyl substituted dipole **3e**, Fig. 2b (red), resulting in a 1,7-electrocyclization for this reactive intermediate (to give benzazepine **6e**); and the lower energy barrier for the 1,5-electrocyclization

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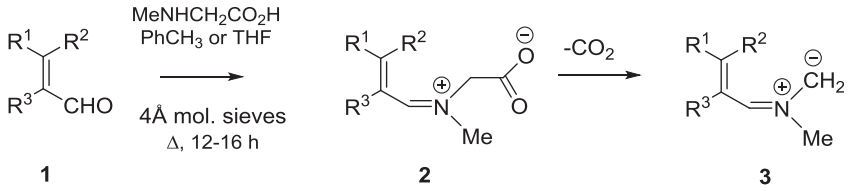
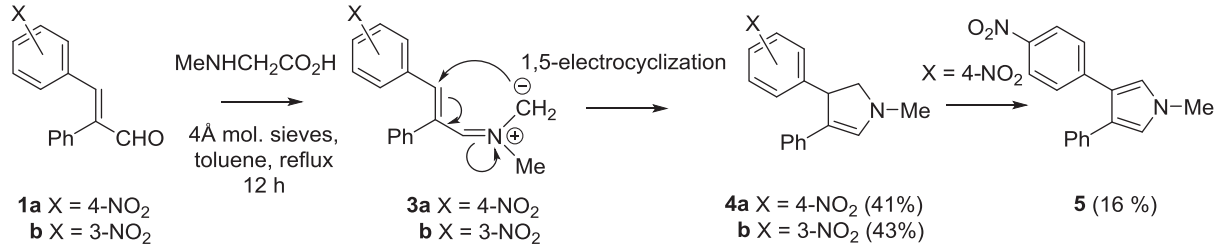
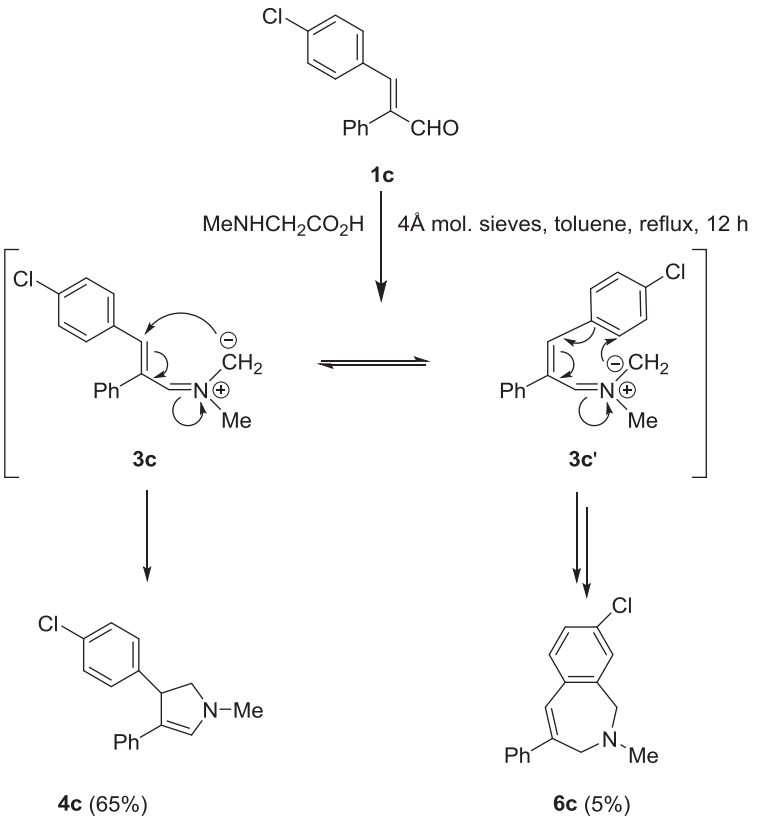
0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.03.078



Scheme 1.





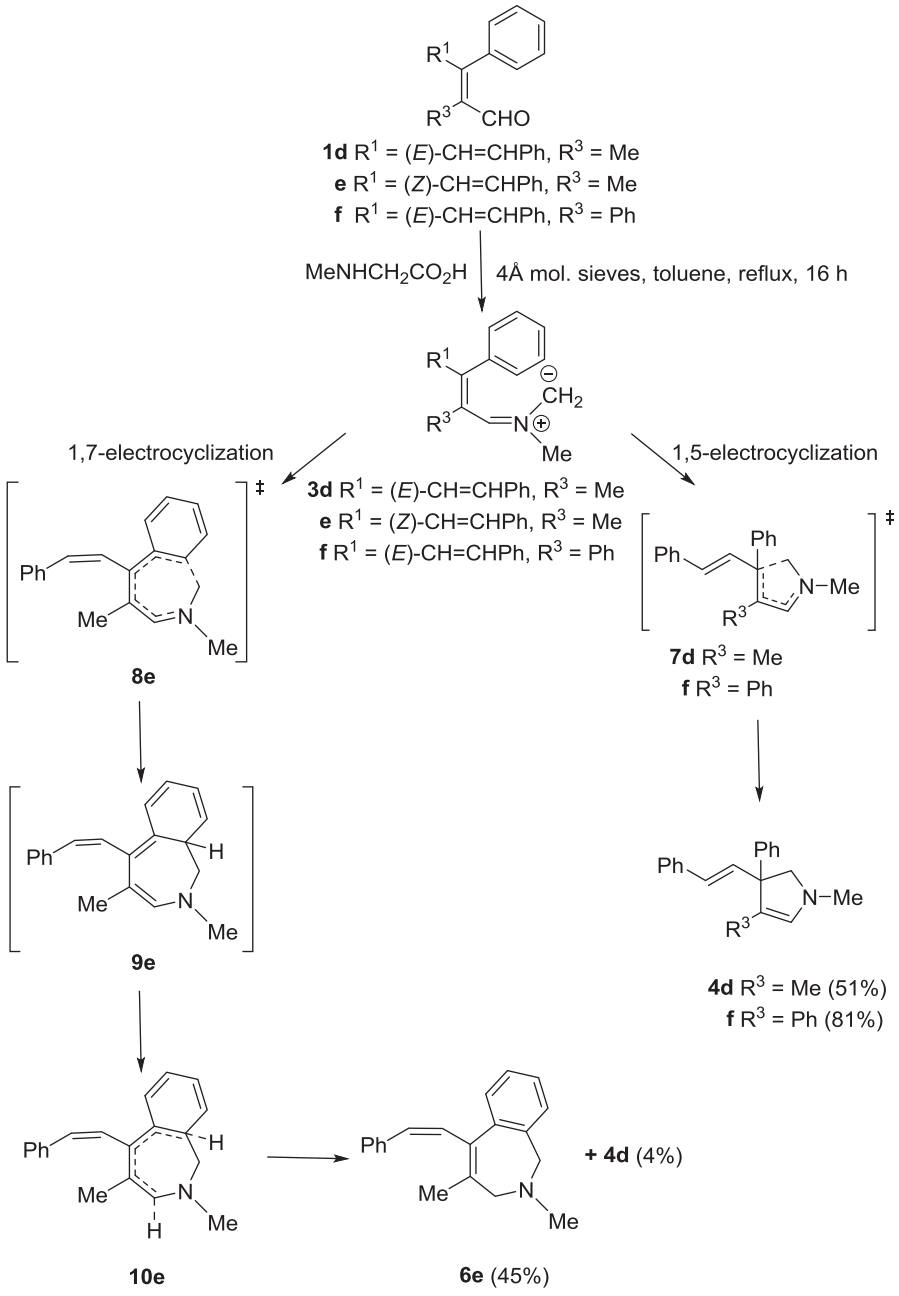
Scheme 2.

of the (*E*)-alkenyl substituted dipole **3d**, Fig. 2a (red), resulting in a 1,5-electrocyclization (to give pyrroline **4d**).

Generation of azomethine ylide **3g** (from aldehyde **1g**) again led to the formation of the benzazepine **6g**, while the bromo derivative **3h** (from **1h**) gave a mixture of the benzazepine **6h** and the pyrrole **11** (formed by a 1,5-electrocyclization to the bromopyrroline followed by dehydrobromination), Scheme 4.

The azomethine ylides **3i**–**l** underwent 1,7-electrocyclization to the dihydroazepines **6i**–**l**, with no evidence for the formation of the pyrroline products of a 1,5-electrocyclization, Scheme 5. The azomethine ylide in which the α,β-bond is the 2,3-position of a thiophene ring **3m** also underwent a 1,7-electrocyclization, to give the dihydrothieno[3,2-*c*]azepine **6m**, Scheme 6, as did the azomethine ylides in which this bond is aromatic **3n-u** (to give the dihydro[2] benzazepines **6n**–**u**), Scheme 7. The intermediacy of azomethine ylides in these processes was shown by the trapping of azomethine ylide **3o** (R=Ph) with *N*-phenylmaleimide to give a single diastereoisomer of the cycloadduct **12**, Scheme 8, with the relative stereochemistry being confirmed by the observation of a NOE between H-2a and H-3.

For the azomethine ylide **3v** (containing a (*Z*)-alkene substituent), no electrocyclization was observed, Scheme 9, while the corresponding (*E*)-alkenyl substituted azomethine ylide **3o** gave the dihydro[2]benzazepine **6o** in good yield. The 1,7-electrocyclization of azomethine ylide **3v** is presumably blocked by the bulky *cis*-phenyl group and more rigid unsaturated system



Scheme 3.

compared to that of **3o**. This blocking effect can be accounted for by the transition state geometry for a 1,7-electrocyclization, resulting in a steric clash between the phenyl group and the nitrogen of the azomethine ylide, as shown in Fig. 3.[8]

Finally, the electrocyclization of the thiophene analogue **3w** involves the disruption of two aromatic rings but the γ,δ-bond, which forms part of the thiophene ring, possesses a reasonable amount of double bond character and the cyclization gives the expected thieno [2,3-*d*][2]benzazepine **6w** in good yield, Scheme 10.

In conclusion, the 1,7-electrocyclization of α,β:γ,δ-conjugated azomethine ylides tolerates a wide range of substituents in the diene component. The nature of the substituents can, in some cases, influence the electrocyclization products obtained, with even very subtle changes having significant effects on the energy barriers for 1,5- versus 1,7-electrocyclizations.

3. Experimental

3.1. General experimental conditions

Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Elemental analyses were performed on a Perkin–Elmer 240C or Carlo Erba 1106 Elemental Analyser.

IR spectra were recorded on a Unicam research series FTIR spectrophotometer using KBr discs or liquid films. ^{1}H NMR spectra were acquired on a JEOL JNM-GSX 270 FT NMR at 270 MHz, or Bruker AVANCE 300 at 300 MHz. Coupling constants are given in Hz and all chemical shifts are relative to an internal standard of tetramethylsilane. ^{13}C NMR spectra were obtained on the JEOL JNM-GFX 270 FT NMR (67.5 MHz) spectrometer and Bruker AVANCE 300 (75 MHz). Low resolution electron impact mass spectra were

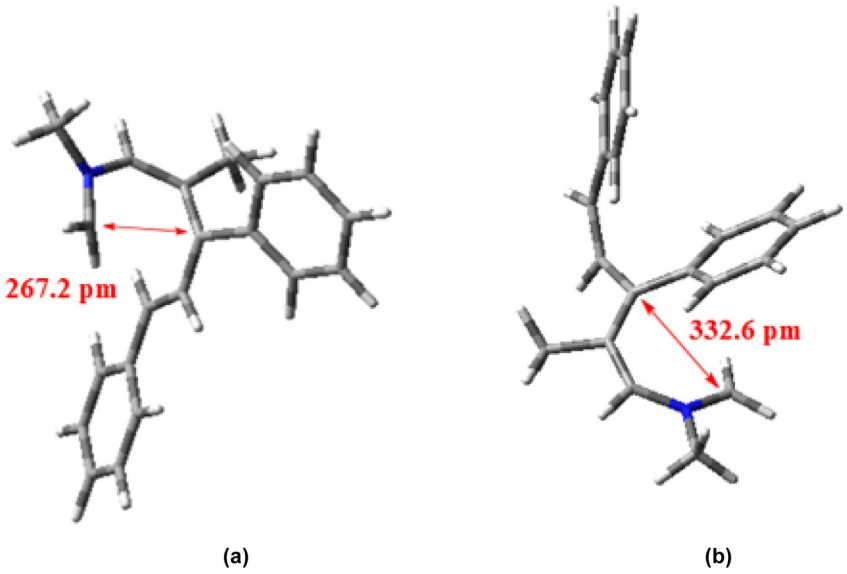


Fig. 1. Calculated transition state **7** distances between the reacting termini for the 1,5-electrocyclization of (a) (*E*)-2′-phenylethenyl **3d** and (b) (*Z*)-2′-phenylethenyl-substituted azomethine ylides **3e**.

Table 1
Relative free energies (B3LYP/6-31G* [kJ mol^{-1}]) for the transition states, intermediates and products of the 1,5- and 1,7-electrocyclizations of dipoles **3e** and **3d**

Reactant		1,5		1,7			
		TS **7**	Product **4**	TS1 **8**	Intermediate **9**	TS2 **10**	Product **6**
3d (*E*)	0	24.8	−130.0	61.1	−48.1	40.9	−132.0
3e (*Z*)	0	120.0	−113.8	66.7	−51.6	34.9	−138.7

obtained on a Trio 2000 VG. High resolution spectra were obtained on a VG ZAB-E spectrometer (E.P.S.R.C. Mass Spectrometry Service Centre, Swansea) or Bruker APEX II FT mass spectrometer.

Thin layer chromatography was performed on Merck silica gel $60F_{254}$. Organic solvents were dried using anhydrous magnesium sulfate and anhydrous sodium sulfate unless otherwise stated. All solvents were purified according to standard procedures. Diethyl ether and tetrahydrofuran were freshly distilled over sodium wire with a trace of benzophenone. Toluene was distilled from, and stored over, sodium wire. Fluka silica gel 60 (230–400 mesh) was used for wet flash chromatography. The samples were applied in liquid form or were pre-adsorbed onto silica 60 (230–400 mesh) from dichloromethane solutions.

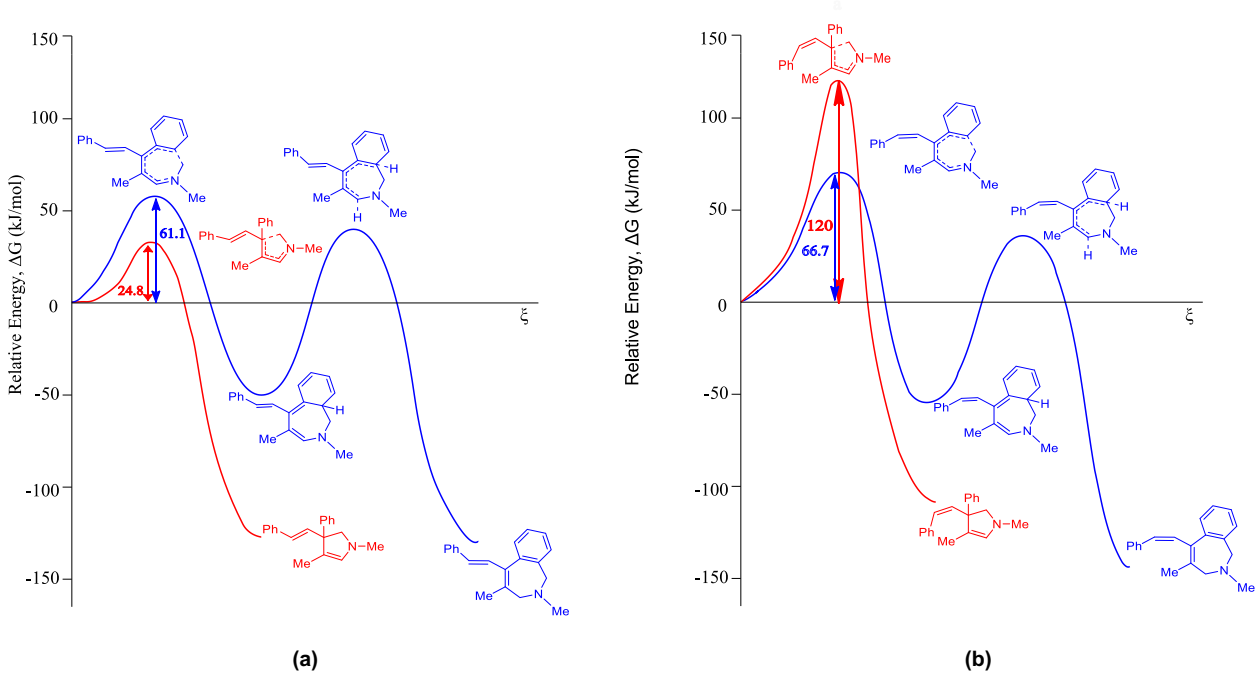
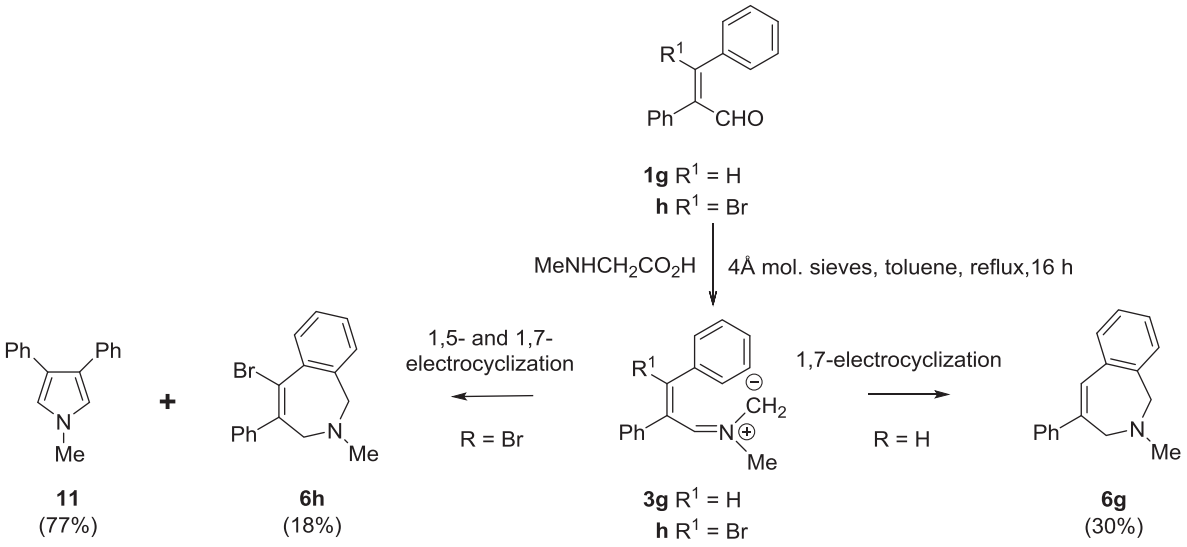
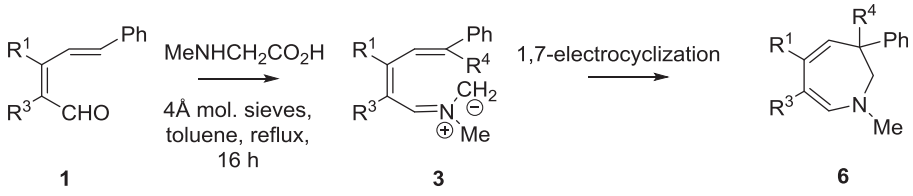


Fig. 2. Reaction profiles for 1,5- (red) and 1,7-electrocyclizations (blue) of; (a) (*E*)-2′-phenylethenyl **3d** and (b) (*Z*)-2′-phenylethenyl **3e** substituted azomethine ylides.

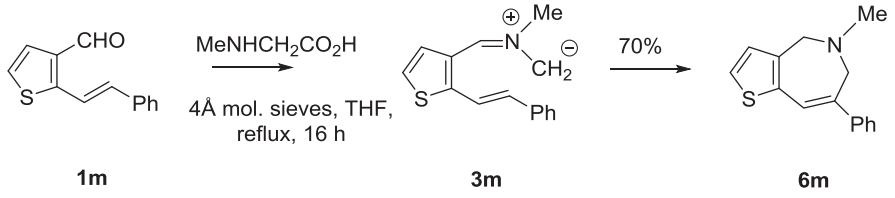


Scheme 4.

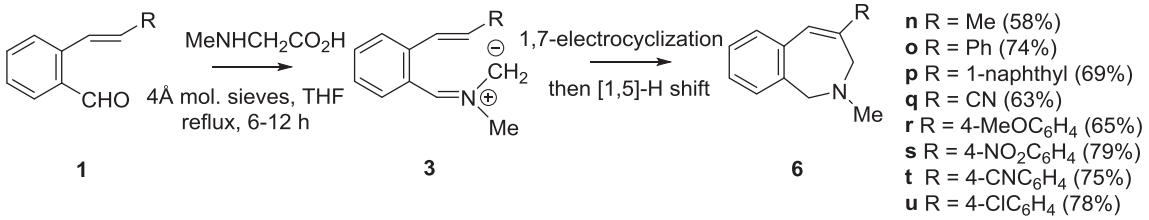


i R^1 = Ph, R^3 = Me, R^4 = H (76%)
j R^1,R^3 = $(CH_2)_3$, R^4 = H (82%)
k R^1,R^3 = $(CH_2)_3$, R^4 = Me (84%)
l R^1,R^3 = $(CH_2)_4$, R_4 = H (78%)

Scheme 5.



Scheme 6.

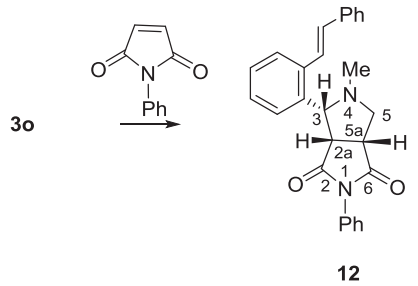


n R = Me (58%)
o R = Ph (74%)
p R = 1-naphthyl (69%)
q R = CN (63%)
r R = 4-$MeOC_6H_4$ (65%)
s R = 4-$NO_2C_6H_4$ (79%)
t R = 4-CNC_6H_4 (75%)
u R = 4-ClC_6H_4 (78%)

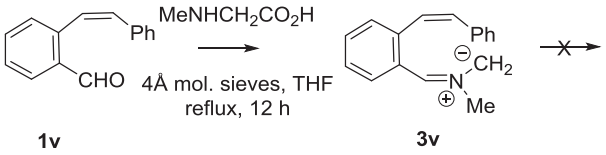
Scheme 7.

3.2. Generation and reaction of azomethine ylides

A mixture of the aldehyde, sarcosine, and 4 Å molecular sieves (2 g) in anhydrous tetrahydrofuran or toluene was heated at reflux, under dry nitrogen, for 12 h. After cooling, the mixture was filtered to remove any solid and the solvent was evaporated under reduced pressure. The residue was purified using column chromatography on silica to give the products.



Scheme 8.



Scheme 9.

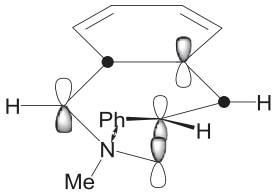
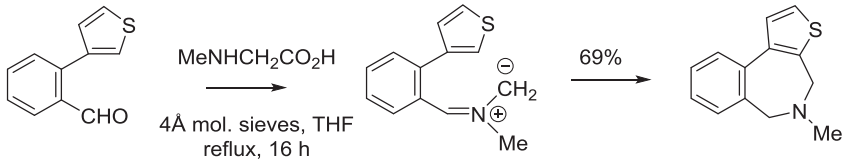


Fig. 3. Transition state geometry for the 1,7-electrocyclization of azomethine ylide **3v**.



Scheme 10.

*3.2.1. 2,3-Dihydro-1-methyl-3-(4-nitrophenyl)-4-phenyl-1H-pyrrole **4a** and 1-methyl-3-(4-nitrophenyl)-4-phenylpyrrole **5**.* The reaction between (*E*)-3-(4-nitrophenyl)-2-phenylpropenal **1a** (0.51 g, 2 mmol) and sarcosine (0.3 g, 3.3 mmol) in toluene (20 mL), was carried out as described above. The solid was removed by filtration and the solvent was evaporated under reduced pressure. Flash chromatography of the residue on silica, eluting with hexane/ethyl acetate (75:25) gave 2,3-dihydro-1-methyl-3-(4-nitrophenyl)-4-phenyl-1*H*-pyrrole **4a** as red needle-like crystals (0.23 g, 41%), mp 102–104 °C; (Found: C, 72.75; H, 5.8; N, 9.9. $C_{17}H_{16}N_2O_2$ requires: C, 72.8; H, 5.75; N, 10.0) (Found: MH^+, 281.128. Calcd for $C_{17}H_{17}N_2O_2$: MH^+, 281.128); ν_{max} (KBr)/cm^{-1} 1594 (C=C), 1507 (NO_2), 1341 (NO_2); ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 2.74 (3H, s, NCH_3), 3.21 (1H, dd, J=9.9 and 4.5 Hz, H-2^a), 3.54 (1H, t, J=9.9 Hz, H-2^b), 4.46 (1H, dd, J=9.9 and 4.5 Hz, H-3), 6.73 (1H, s, H-5), 7.00–7.04 (5H, m), 7.12 (2H, d, J=9.0 Hz), 7.40 (2H, d, J=9.0 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 40.0 (CH_3), 49.8 (CH), 64.4 (CH_2), 117.6 (quat), 123.9 (2× CH), 124.4 (2× CH), 125.0 (2× CH), 128.8 (2× CH), 130.0 (CH), 135.3 (quat), 140.7 (CH), 147.3 (quat), 152.3 (quat); and 1-methyl-3-(4-nitrophenyl)-4-phenylpyrrole **5** as a brown oil (90 mg, 16%); (found: MH^+, 279.113. Calcd for $C_{17}H_{15}N_2O_2$: MH^+, 279.113); ν_{max} (liquid film)/cm^{-1} 1594 (C=C), 1513 (NO_2), 1348 (NO_2); ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 3.65 (3H, s, NCH_3), 6.64 (1H, d, J=2.4 Hz, =CH), 6.77 (1H, d, J=2.4 Hz, =CH), 7.12–7.18 (5H, m, Ar–H), 7.25 (2H, d, J=9.0 Hz), 7.97 (2H, d, J=9.0 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 36.8 (NCH_3), 121.7 (quat) 122.7 (CH), 122.8 (CH), 124.1 (2× CH), 124.5 (quat), 126.7 (CH) 128.4 (2× CH), 128.8 (2× CH), 129.1 (2× CH), 135.5 (quat), 143.5 (quat), 145.8 (quat).

*3.2.2. 2,3-Dihydro-1-methyl-3-(3-nitrophenyl)-4-phenyl-1H-pyrrole **4b**.* This was prepared, as above, from (*E*)-3-(3-nitrophenyl)-2-phenylpropenal **1b** (0.51 g, 2 mmol), sarcosine (0.3 g, 3.3 mmol) in toluene (20 mL), to give 2,3-dihydro-1-methyl-3-(3-nitrophenyl)-4-phenyl-1*H*-pyrrole **4b** as a brown oil (0.24 g, 43%); (found: MH^+, 281.128. Calcd for $C_{17}H_{17}N_2O_2$: MH^+, 281.128); ν_{max} (liquid film)/cm^{-1} 1608 (C=C), 1525 (NO_2), 1346 (NO_2); ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 2.63 (3H, s, NCH_3), 3.12 (1H, dd, J=9.9 and 3.9 Hz, H-2^a), 3.42 (1H, t, J=9.9 Hz, H-2^b), 4.35 (1H, dd, J=9.9 and 3.9 Hz, H-3), 6.64 (1H, s, =CH, H-5), 6.87–8.10 (9H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 39.9 (CH_3), 49.6 (CH), 64.5 (CH_2), 117.5 (quat), 122.1 (CH), 123.0 (CH), 123.9 (2× CH), 124.9 (CH), 128.8 (2× CH), 129.9 (CH), 1134.2 (CH), 135.3 (quat), 140.9 (CH), 1146.7 (quat), 149.1 (quat).

*3.2.3. 3-(4-Chlorophenyl)-2,3-dihydro-1-methyl-4-phenyl-1H-pyrrole **4c** and 8-chloro-2,3-dihydro-2-methyl-4-phenyl-1H-2-benzazepine **6c**.* (*E*)-3-(4-Chlorophenyl)-2-phenylpropenal **1c** (0.7 g, 2.9 mmol) was reacted with sarcosine (0.4 g, 4.4 mmol) in toluene (20 mL) as described above. Removal of the solid, by filtration, and the solvent by evaporation under reduced pressure, gave a residue, which was separated by column chromatography on silica, eluting with petroleum ether (60–80 °C)/ether (75:25) to give 3-(4-chlorophenyl)-2,3-dihydro-1-methyl-4-phenyl-1*H*-pyrrole **4c** as a yellow oil (0.51 g, 65%); (found: MH^+, 270.105. Calcd for $C_{17}H_{17}{}^{35}ClN$: MH^+, 270.104); ν_{max} (liquid film)/cm^{-1} 1609 (C=C), 1487 (C=C); ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 2.72 (3H, s, NCH_3), 3.16 (1H, dd, J=9.6 and 4.8 Hz, H^a-2), 3.54 (1H, dd, J=9.9 and 9.6 Hz, H^b-2), 4.46 (1H, ddd, J=9.6, 4.8 and 0.9 Hz, H-3), 6.69 (1H, d, J=0.9 Hz, 5-H), 6.78–7.27 (9H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 40.1 (CH_3), 49.4 (CH), 64.9 (CH_2), 117.9 (quat), 124.0 (2× CH), 124.7 (CH), 128.7 (2× CH), 129.1 (2× CH), 129.4 (2× CH), 132.5 (quat), 135.8 (quat), 140.4 (CH), 143.0 (quat); and 8-chloro-2,3-dihydro-2-methyl-4-phenyl-1*H*-2-benzazepine **6c** as a yellow oil (40 mg, 5%); (found: MH^+, 270.105. Calcd for $C_{17}H_{17}{}^{35}ClN$: MH^+, 270.104); ^{1}H NMR (270 MHz, $CDCl_3$) δ ppm 2.41 (3H, s, NCH_3), 3.70 (2H, s), 3.75 (2H, s), 6.69 (1H, s, H-5), 7.10–7.40 (8H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 43.2 (CH_3), 60.3 (CH_2), 60.9 (CH_2), 126.8 (2× CH), 127.7 (CH), 128.1 (CH), 128.8 (CH), 128.9 (2× CH), 129.4 (CH), 132.3 (CH), 133.0 (quat), 135.8 (quat), 139.5 (quat), 142.2 (quat), 142.7 (quat).

*3.2.4. (1′E)-2,3-Dihydro-1,4-dimethyl-3-phenyl-3-(2′-phenylethenyl)-1H-pyrrole **4d**.* The reaction between a mixture of (2*Z*,4*E*)- and (2*Z*,4*Z*)-2-methyl-3,5-diphenylpenta-2,4-dienal **1d** and **1e** (3:1, 0.50 g, 2.02 mmol), and sarcosine (0.36 g, 4.04 mmol) was carried out in toluene (50 mL) for 16 h, as described above. The solid was removed by filtration and the solvent was evaporated under reduced pressure. Flash chromatography of the residue on silica, eluting with hexane/ethyl acetate (90:10 to 70:30), gave (*E*)-2,3-dihydro-1,4-dimethyl-3-phenyl-3-(2′-phenylethenyl)-1*H*-pyrrole

4d as a pale yellow oil (0.28 g, 51%); (found: MH^+, 276.175. Calcd for $C_{20}H_{22}N$: MH^+, 276.175); ν_{max} (liquid film)/cm^{-1} 1599 (C=C), 1493 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.62 (3H, d, J=1.3 Hz, CH_3), 2.54 (3H, s, NCH_3), 3.12 (1H, d, J=9.9 Hz, H-2[a]), 3.43 (1H, d, J=9.9 Hz, H-2[b]), 5.78 (1H, q, J=1.3 Hz, =CH, H-5), 6.48 (1H, d, J=16.5 Hz, =CH), 6.58 (1H, d, J=16.5 Hz, =CH), 7.18–7.49 (10H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 10.6 (CH_3), 41.1 (NCH_3), 59.6 (quat), 69.7 (CH_2), 116.6 (quat), 126.26 (CH), 126.31 (2× CH), 127.1 (CH), 127.70 (2× CH), 128.3 (2× CH), 128.5 (2× CH), 128.9 (CH), 133.1 (CH), 137.6 (quat), 138.6 (CH), 145.2 (quat).

*3.2.5. (1′E)-2,3-Dihydro-1-methyl-3,4-diphenyl-3-(2′-phenylethenyl)-1H-pyrrole **4f**.* The reaction between a mixture of (2*Z*,4*E*)-2,3,5-triphenylpenta-2,4-dienal **1f** (0.50 g, 1.61 mmol), sarcosine (0.28 g, 3.15 mmol) was carried out in toluene (50 mL), as described above. After cooling to room temperature, the mixture was filtered to remove any solid. Evaporation of the solvent under reduced pressure gave (*E*)-2,3-dihydro-1-methyl-3,4-diphenyl-3-(2′-phenyl-ethenyl)-1*H*-pyrrole **4f** as a yellow oil (0.44 g, 81%); (found: MH^+, 338.191. Calcd for $C_{25}H_{24}N$: MH^+, 338.190); ν_{max} (liquid film)/cm^{-1} 1599 (C=C), 1495 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.72 (3H, s, NCH_3), 3.23 (1H, d, J=8.6 Hz, H-2[a]), 3.68 (1H, d, J=8.6 Hz, H-2[b]), 6.63 (1H, d, J=16.5 Hz, =CH), 6.67 (1H, s, =CH, H-5), 6.87 (1H, d, J=16.5 Hz, =CH), 7.09–7.32 (11H, m, Ar–H), 7.38 (2H, m, Ar–H), 7.49 (2H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 39.7 (CH_3), 58.6 (quat), 71.1 (CH_2), 118.8 (quat), 124.0 (CH), 124.7 (2× CH), 126.40 (CH), 126.43 (2× CH), 127.2 (CH), 127.8 (2× CH), 128.1 (2× CH), 128.3 (2× CH), 128.5 (2× CH), 129.4 (CH), 132.8 (CH), 135.2 (quat), 137.6 (quat), 140.5 (CH), 145.5 (quat).

*3.2.6. (1′Z)-2,3-Dihydro-2,4-dimethyl-5-(2′-phenylethenyl)-1H-2-benzazepine **6e**.* The reaction between (2*Z*,4*Z*)- and (2*Z*,4*E*)-2-methyl-3,5-diphenylpenta-2,4-dienal **1e** and **1d** (3:1, 0.30 g, 1.2 mmol), and sarcosine (0.22 g, 2.4 mmol) was carried out in toluene (50 mL), as described above. The solid was removed by filtration and the solvent was evaporated under reduced pressure. Flash chromatography of the residue on silica, eluting with hexane/ethyl acetate (90:10 to 70:30), gave (*Z*)-2,3-dihydro-2,4-dimethyl-5-(2′-phenylethenyl)-1*H*-2-benzazepine **6e** as a pale yellow oil (0.15 g, 45%); (Found: MH^+, 276.175. Calcd for $C_{20}H_{22}N$: MH^+, 276.175); ν_{max} (liquid film)/cm^{-1} 1597 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.92 (3H, s, CH_3), 2.46 (3H, s, NCH_3), 2.79 (2H, s, CH_2), 3.55 (2H, s, CH_2), 6.29 (1H, d, J=12.3 Hz, =CH), 6.33 (1H, d, J=12.3 Hz, =CH), 7.12-7.27 (9H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 22.6 (CH_3), 44.0 (NCH_3), 58.5 (CH_2), 58.7 (CH_2), 127.3 (CH), 127.41 (CH), 127.7 (CH), 127.9 (CH), 128.3 (2× CH), 128.7 (2× CH), 129.0 (CH), 130.1 (CH), 132.5 (CH), 134.1 (quat), 135.6 (quat), 135.9 (quat), 138.0 (quat), 141.1 (quat) and (*E*)-2,3-dihydro-1,4-dimethyl-3-phenyl-3-(2′-phenylethenyl)-1*H*-pyrrole **4d** (0.013 g, 4%) for which the spectroscopic data was identical to that presented above.

*3.2.7. 2,3-Dihydro-2-methyl-4-phenyl-1H-2-benzazepine **6g**.* A mixture of (*Z*)-2,3-diphenyl-2-propenal **1g** (0.1 g, 0.5 mmol) and sarcosine (0.1 g, 1.1 mmol) in anhydrous toluene (20 mL) was heated at reflux overnight as described above. After cooling to room temperature, the mixture was filtered to remove any solid. The solvent was evaporated under reduced pressure and the residue was separated by column chromatography on silica, eluting with ether/ethyl acetate (90 : 10) to give 2,3-dihydro-2-methyl-4-phenyl-1*H*-2-benzazepine **6g** as a yellow oil (35 mg, 30%); (found: MH^+, 236.144. Calcd for $C_{17}H_{18}N$: MH^+, 236.143); ν_{max} (KBr)/cm^{-1} 1490 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.42 (3H, s, NCH_3), 3.67 (2H, s), 3.78 (2H, s), 6.78 (1H, s, H-5), 7.12–7.43 (9H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 43.4 (CH_3), 60.5 (CH_2), 60.6 (CH_2), 126.8 (2× CH), 127.6 (CH), 127.8 (CH), 127.9 (CH), 128.9 (2× CH), 129.6 (CH), 130.0 (CH), 130.9 (CH), 137.4 (quat), 137.5 (quat), 141.3 (quat), 142.9 (quat).

*3.2.8. 5-Bromo-2,3-dihydro-2-methyl-4-phenyl-1H-2-benzazepine **6h** and 1-methyl-3,4-diphenylpyrrole **11**.* (*E*)-3-Bromo-2,3-diphenyl-2-propenal **1h** (0.4 g, 1.4 mmol) was reacted with sarcosine (0.25 g, 2.8 mmol) as described above. The solid was removed by filtration and the solvent by evaporation under reduced pressure and the residue was separated by column chromatography on silica, eluting with hexane/ethyl acetate (75 : 25) to give 1-methyl-3,4-diphenylpyrrole **11** (0.25 g, 77%), mp 122–124 °C (lit.[9] 124–126 °C); (Found: C, 87.5; H, 6.5; N, 5.9. $C_{17}H_{15}N$ requires: C, 87.5; H, 6.48; N, 6.0) (found: MH^+, 234.129. Calcd for $C_{17}H_{16}N$: MH^+, 234.128); ν_{max} (KBr)/cm^{-1} 1539 (C=C), 1483 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 3.54 (3H, s, NCH_3), 6.55 (2H, s), 6.97–7.10 (10H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 36.7 (CH_3), 121.7 (2× CH), 123.9 (2× quat), 125.9 (2× CH), 128.5 (4× CH), 128.8 (4× CH), 136.3 (2× quat); and 5-bromo-2,3-dihydro-2-methyl-4-phenyl-1*H*-2-benzazepine **6h** as a colourless crystals (80 mg, 18%); mp 85–87 °C; (found: MH^+, 314.055 and 316.054. Calcd for $C_{17}H_{17}NBr$: MH^+, 314.054 and 316.052); ν_{max} (KBr)/cm^{-1} 1491 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.30 (3H, s, NCH_3), 3.08 (2H, s), 3.62 (2H, s), 7.17–7.67 (9H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 43.9 (CH_3), 58.4 (CH_2), 59.2 (CH_2), 121.9 (quat), 127.9 (CH), 128.3 (CH), 128.6 (2× CH), 128.7 (2× CH), 129.2 (CH), 129.8 (CH), 129.9 (CH), 135.6 (quat), 140.1 (quat), 141.0 (quat), 143.4 (quat).

*3.2.9. 2,3-Dihydro-1,6-dimethyl-3,5-diphenyl-1H-azepine **6i**.* A mixture of (2*E*,4*E*)-3,5-diphenyl-2-methylpenta-2,4-dienal **1i** (0.50 g, 2.02 mmol), sarcosine (0.36 g, 4.04 mmol) in toluene (70 mL) was heated at reflux overnight, as described above. After cooling to room temperature, the mixture was filtered to remove any solid. Evaporation of the solvent under reduced pressure gave 2,3-dihydro-1,6-dimethyl-3,5-diphenyl-1*H*-azepine **6i** as a yellow oil (0.42 g, 76%); (found: MH^+, 276.174. Calcd for $C_{20}H_{22}N$: MH^+, 276.175); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.63 (3H, s, CH_3), 2.73 (3H, s, NCH_3), 3.35 (2H, m, CH_2), 3.53 (1H, m, H-3), 5.76 (1H, d, J=4.6 Hz, =CH, H-4), 6.16 (1H, s, =CH, H-7), 7.14–7.29 (10H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 22.7 (CH_3), 45.5 (CH), 47.8 (NCH_3), 64.1 (CH_2), 102.5 (quat), 126.1 (CH), 126.2 (CH), 127.6 (4× CH), 128.4 (2× CH), 128.5 (2× CH), 131.1 (CH), 138.7 (CH), 142.4 (quat), 144.2 (quat), 144.6 (quat).

*3.2.10. 3,4,6,7,8-Pentahydro-2-methyl-4-phenyl-2H-cyclopenta[c]azepine **6j**.* (1′*E*)-1-Formyl-2-(2′-phenylethenyl)cyclopentene **1j** (0.50 g, 2.53 mmol) was reacted with sarcosine (0.45 g, 5.06 mmol) as described above. Removal of the solid by filtration and the solvent by evaporation under reduced pressure gave 3,4,6,7,8-pentahydro-2-methyl-4-phenyl-2*H*-cyclopenta[*c*]azepine **6j** as a yellow oil (0.47 g, 82%); (found: MH^+, 226.159. Calcd for $C_{16}H_{20}N$: MH^+, 226.159); ν_{max} (liquid film)/cm^{-1} 1604 (C=C), 1492 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.67 (2H, m, CH_2), 2.49 (4H, m, 2× CH_2), 2.61 (3H, s, NCH_3), 3.02 (1H, dd, J=12.5 and 5.9 Hz, H-3[a]), 3.22 (1H, dd, J=12.5 and 2.0 Hz, H-3[b]), 3.57 (1H, m, H-4), 5.53 (1H, d, J=4.0 Hz, =CH, H-5), 6.12 (1H, s, =CH, H-1), 7.11–7.29 (5H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 25.6 (CH_2), 34.1 (CH_2), 37.1 (CH_2), 44.3 (CH), 48.8 (NCH_3), 60.1 (CH_2), 111.6 (quat), 119.6 (CH), 125.9 (CH), 127.7 (2× CH), 128.1 (2× CH), 134.5 (CH), 141.4 (quat), 144.8 (quat).

*3.2.11. 3,4,6,7,8-Pentahydro-2,4-dimethyl-4-phenyl-2H-cyclopenta[c]azepine **6k**.* The reaction between (1′*E*)-1-formyl-2-(2′-methyl-2′-phenylethenyl)cyclopentene **1k** (0.65 g, 3.07 mmol) and sarcosine (0.55 g, 6.18 mmol) using the method above gave 3,4,6,7,8-pentahydro-2,4-dimethyl-4-phenyl-2*H*-cyclopenta[*c*]azepine **6k** as a brown oil (0.61 g, 84%); (found: MH^+, 240.174. Calcd for

$C_{17}H_{22}N$: MH^+, 240.175); ν_{max} (liquid film)/cm^{-1} 1608 (C=C), 1493 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.48 (3H, s, CH_3), 1.78 (2H, m, CH_2), 2.62–2.66 (4H, m, 2× CH_2), 2.66 (3H, s, NCH_3), 3.12 (2H, s, NCH_2), 5.47 (1H, s, =CH), 6.12 (1H, s, =CH), 7.21–7.39 (5H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 25.65 (CH_3), 25.70 (CH_2), 34.2 (CH_2), 37.3 (CH_2), 44.8 (NCH_3), 48.1 (quat), 65.9 (NCH_2), 109.9 (quat), 124.0 (CH), 125.6 (CH), 126.7 (2× CH), 127.8 (2× CH), 134.8 (CH), 139.7 (quat), 147.5 (quat).

3.2.12. 3,4,6,7,8,9-Hexahydro-2-methyl-4-phenyl-2H-2-benzazepine ***6l***. This was prepared, as above, from (1'*E*)-1-formyl-2-(2′-phenylethenyl)cyclohexene **1l** (0.70 g, 3.30 mmol), sarcosine (0.59 g, 6.63 mmol) and anhydrous toluene (70 mL), to give 3,4,6,7,8,9-hexahydro-2-methyl-4-phenyl-2*H*-2-benzazepine **6l** as a deep blue oil (0.62 g, 78%); (found: MH^+, 240.175. Calcd for $C_{17}H_{22}N$: MH^+, 240.175); ν_{max} (liquid film)/cm^{-1} 1602 (C=C), 1493 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.72 (4H, m, 2× CH_2), 2.15 (4H, m, 2× CH_2), 2.63 (1H, m, H-4), 2.67 (3H, s, NCH_3), 3.03 (1H, dd, J=14.5 and 6.6 Hz, H-3[a]), 3.26 (1H, dd, J=14.5 and 7.9 Hz, H-3[b]), 5.26 (1H, d, J=3.3 Hz, =CH, H-5), 5.70 (1H, s, =CH, H-1), 7.11–7.29 (5H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 24.2 (CH_2), 26.3 (CH_2), 31.2 (CH_2), 43.7 (CH_2), 45.2 (CH), 45.9 (NCH_3), 63.5 (NCH_2), 110.6 (quat), 121.3 (CH), 126.1 (CH), 126.9 (2× CH), 128.2 (2× CH), 135.5 (quat), 136.8 (CH), 146.3 (quat).

3.2.13. 2,3-Dihydro-2-methyl-4-phenyl-1H-thieno[3,2-c]azepine ***6m***. This was prepared, as above, from (1'*E*)-2-(2′-phenylethenyl) thiophene-3-carboxaldehyde **1m** (0.50 g, 2.34 mmol), sarcosine (0.32 g, 3.60 mmol) in dry THF (70 mL) with refluxing for 12 h. The usual work-up as above and chromatography on silica, eluting with petroleum ether 60–80 °C/diethyl ether (70:30) gave 2,3-dihydro-2-methyl-4-phenyl-1*H*-thieno[3,2-*c*]azepine **6m** as a brown oil (0.39 g, 70%); (found: MH^+, 242.100. Calcd for $C_{15}H_{16}NS$, MH^+, 242.100); ν_{max} (liquid film)/cm^{-1} 1594 (C=C), 1492 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.81 (3H, s, NCH_3), 3.99 (2H, s, CH_2), 4.18 (2H, s, CH_2), 6.06 (1H, s, =CH, H-5), 6.85 (1H, d, J=5.3 Hz, H-7), 6.95 (1H, d, J=5.3 Hz, H-6), 7.11 (1H, m, Ar–H), 7.24 (4H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 29.2 (NCH_3), 45.3 (CH_2), 50.8 (CH_2), 110.6 (quat), 120.3 (CH), 124.8 (CH), 125.1 (2× CH), 128.0 (CH), 128.2 (2× CH), 134.0 (quat), 138.2 (quat), 139.2 (CH), 144.7 (quat).

3.2.14. 2,3-Dihydro-2,4-dimethyl-1H-2-benzazepine ***6n***. (1'*E*)-1-Formyl-2-(1′-prop-1′-enyl)benzene **1n** (0.45 g, 3.08 mmol) was reacted with sarcosine (0.55 g, 6.18 mmol) in dry THF (50 mL) using the method above, to give, after column chromatography on neutral aluminium oxide eluting with hexane/ether (90:1), 2,3-dihydro-2,4-dimethyl-1*H*-2-benzazepine as a pale yellow oil **6n** (0.31 g, 58%); (found: MH^+, 174.129. Calcd for $C_{12}H_{16}N$: MH^+, 174.128); ν_{max} (liquid film)/cm^{-1} 1661 (C=C), 1606 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 1.66 (3H, s, CH_3), 2.43 (3H, s, NCH_3), 3.36 (2H, s, CH_2), 4.06 (2H, s, CH_2), 5.39 (1H, s, =CH, H-5), 6.93–7.21 (4H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 24.5 (CH_3), 36.9 (NCH_3), 42.2 (CH_2), 55.2 (CH_2), 107.6 (quat), 125.8 (CH), 127.1 (CH), 127.8 (CH), 127.9 (CH), 133.5 (CH), 135.6 (quat), 140.9 (quat).

3.2.15. 2,3-Dihydro-2-methyl-4-phenyl-1H-2-benzazepine ***6o***. This was prepared, as described above, from a mixture of (1'*E*)-1-formyl-2-(2′-phenylethenyl)benzene **1o** (0.42 g, 2.02 mmol) and sarcosine (0.27 g, 3.03 mmol) in THF (70 mL) to give, after column chromatography on silica eluting with hexane/ethyl acetate (90:10), 2,3-dihydro-2-methyl-4-phenyl-1*H*-2-benzazepine **6o** as a brown oil (0.35 g, 74%); (found: MH^+, 236.143. Calcd for $C_{17}H_{18}N$: MH^+, 236.143); ν_{max} (liquid film)/cm^{-1} 1631 (C=C), 1592 (C=C), 1492 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.72 (3H, s, NCH_3), 3.94 (2H, s, CH_2), 4.28 (2H, s, CH_2), 5.88 (1H, s, =CH, H-5), 7.05–7.28 (9H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 35.1 (NCH_3) 43.7 (CH_2), 54.9 (CH_2), 110.0 (quat), 124.4 (CH), 125.1 (2× CH), 126.5 (CH), 127.9 (CH), 128.0 (CH), 128.05 (CH), 128.1 (2× CH), 135.4 (quat), 137.5 (CH), 141.3 (quat), 144.9 (quat).

3.2.16. 2,3-Dihydro-4-(1′-naphthyl)-2-methyl-1H-2-benzazepine ***6p***. This was prepared, as described above, from a mixture of (1'*E*)-1-formyl-2-[2′-(1″-naphthyl)ethenyl]benzene **1p** (0.85 g, 3.29 mmol) and sarcosine (0.44 g, 4.94 mmol) in THF (70 mL). The usual work-up, and chromatography on silica, eluting with petroleum ether 60–80 °C/diethyl ether (90 : 10), gave 2,3-dihydro-2-methyl-4-(1′-naphthyl)-1*H*-2-benzazepine as a pale yellow oil **6p** (0.65 g, 69%); (found: MH^+, 286.159. Calcd for $C_{21}H_{20}N$: MH^+, 286.159); ν_{max} (liquid film)/cm^{-1} 1597 (C=C), 1574 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.58 (3H, s, NCH_3), 3.81 (2H, s, CH_2), 4.28 (2H, s, CH_2), 5.67 (1H, s, =CH, H-5), 7.10 (1H, m, Ar–H), 7.19 (1H, m, Ar–H), 7.23–7.44 (5H, m, Ar–H), 7.61–7.80 (3H, m, Ar–H), 8.20 (1H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 37.4 (NCH_3), 43.0 (CH_2), 54.9 (CH_2), 110.4 (quat), 125.31 (CH), 125.33 (CH), 125.5 (CH), 126.1 (CH), 126.3 (CH), 126.37 (CH), 126.43 (CH), 127.8 (CH), 127.9 (CH), 128.2 (CH), 128.3 (CH), 131.9 (quat), 133.9 (quat), 135.7 (quat), 138.0 (CH), 141.8 (quat), 143.6 (quat).

3.2.17. 4-Cyano-2,3-dihydro-2-methyl-1H-2-benzazepine ***6q***. The reaction between (1'*E*)-2-(2′-cyanoethenyl)benzaldehyde **1q** (0.50 g, 3.18 mmol) and sarcosine (0.43 g, 4.83 mmol) in THF (70 mL), as described above, gave, after column chromatography on neutral aluminium oxide, eluting with hexane/ether (75:25), 2,3-dihydro-2-methyl-4-cyano-1*H*-2-benzazepine **6q** as a pale yellow oil (0.37 g, 63%); (found: MH^+, 185.108. Calcd for $C_{12}H_{13}N_2$: MH, 185.107); ν_{max} (liquid film)/cm^{-1} 2177 (C≡N), 1624 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.96 (3H, s, NCH_3), 3.64 (2H, s, CH_2), 4.36 (2H, s, CH_2), 6.41 (1H, s, =CH, H-5), 7.13–7.30 (4H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 32.2 (NCH_3), 44.6 (CH_2), 54.0 (CH_2), 102.4 (quat), 124.6 (CN), 127.3 (CH), 128.1 (CH), 128.5 (CH), 128.9 (CH), 134.5 (quat), 139.9 (quat), 149.5 (CH).

3.2.18. 2,3-Dihydro-4-(4′-methoxyphenyl)-2-methyl-1H-2-benzazepine ***6r***. (1'*E*)-1-Formyl-2-[2′-(4″-methoxyphenyl) ethenyl]benzene **1r** (0.70 g, 2.94 mmol) was reacted with sarcosine (0.39 g, 4.38 mmol) as above to give, after column chromatography on neutral aluminium, eluting with petroleum (60–80 °C)/diethyl ether (90:10), 2,3-dihydro-2-methyl-4-(4′-methoxyphenyl)-1*H*-2-benzazepine **6r** as a pale yellow oil (0.50 g, 65%); (found: MH^+, 266.154. Calcd for $C_{18}H_{20}NO$: MH, 266.154); ν_{max} (liquid film)/cm^{-1} 1604 (C=C), 1576 (C=C), 1512 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.69 (3H, s, NCH_3), 3.75 (3H, s, OCH_3), 3.91 (2H, s, CH_2), 4.27 (2H, s, CH_2), 5.78 (1H, s, = CH, H-5), 6.81 (2H, d, J=8.6 Hz, H-3′,5′), 7.12–7.21 (6H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 35.6 (NCH_3), 43.5 (CH_2), 55.0 (CH_2), 55.2 (OCH_3), 110.4 (quat), 113.5 (2× CH), 126.36 (2× CH), 126.39 (CH), 127.8 (CH), 128.0 (2× CH), 135.5 (quat), 136.4 (CH), 137.7 (quat), 141.4 (quat), 157.1 (quat).

3.2.19. 2,3-Dihydro-2-methyl-4-(4′-nitrophenyl)-1H-2-benzazepine ***6s***. This was prepared from a mixture of (1'*E*)-2-[2′-(4″-nitrophenyl)ethenyl]benzaldehyde **1s** (0.35 g, 1.38 mmol) and sarcosine (0.18 g, 2.02 mmol), in THF (50 mL) was refluxed for 6 h. Work-up as above and column chromatography on silica, eluting with petroleum 60–80 °C/diethyl ether (70 : 30), gave 2,3-dihydro-2-methyl-4-(4′-nitrophenyl)-1*H*-2-benzazepine **6s** as a red oil (0.31 g, 79%); (found: MH^+, 281.129. Calcd for $C_{17}H_{17}N_2O_2$: MH, 281.128); ν_{max} (liquid film)/cm^{-1} 1621 (C=C), 1572 (N=O), 1319 (N=O); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.95 (3H, s, NCH_3), 3.97 (2H, s, CH_2), 4.41 (2H, s, CH_2), 6.25 (1H, s, =CH, H-5), 7.17–7.32 (6H, m, Ar–H), 8.08 (2H, d, J=9.2 Hz, H-3′,5′); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 34.0 (NCH_3), 44.6 (CH_2), 54.7 (CH_2), 105.9 (quat), 123.6 (2× CH), 124.0

(2× CH) 127.0 (CH), 128.0 (CH), 128.2 (CH), 128.5 (CH), 135.0 (quat), 140.5 (quat), 140.9 (CH), 143.6 (quat), 151.7 (quat).

3.2.20. 4-(4′-Cyanophenyl)-2,3-dihydro-2-methyl-1H-2-benzazepine ***6t***. A mixture of (1′*E*)-2-[2′-(4′′-cyanophenyl)ethenyl]benzaldehyde **1t** (0.50 g, 3.18 mmol) and sarcosine (0.43 g, 4.83 mmol) in dry THF (70 mL) was refluxed for 8 h. The work-up as above and chromatography on silica, eluting with petroleum ether 60–80 °C/diethyl ether (75:25) gave 2,3-dihydro-2-methyl-4-(4′-cyanophenyl)-1*H*-2-benzazepine **6t** as a pale yellow oil (0.44 g, 75%); (found: MH^+, 261.139. Calcd for $C_{18}H_{17}N_2$: MH, 261.139); ν_{max} (liquid film)/cm^{-1} 2218 (C≡N), 1587 (C=C), 1502 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.89 (3H, s, *N*CH_3), 3.93 (2H, s, CH_2), 4.38 (2H, s, CH_2), 6.11 (1H, s, =CH, H-5), 7.18–7.26 (4H, m, Ar–H), 7.29 (2H, d, *J*=8.9 Hz, Ar–H), 7.49 (2H, d, *J*=8.9 Hz, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 34.1 (CH_3), 44.3 (CH_2), 54.7 (CH_2), 106.5 (CN), 119.8 (quat), 124.4 (2× CH), 126.9 (CH), 128.0 (CH), 128.2 (CH), 128.3 (CH), 128.7 (quat), 132.1 (2× CH), 135.1 (quat), 140.0 (CH), 140.7 (quat), 149.5 (quat).

3.2.21. 4-(4′-Chlorophenyl)-2,3-dihydro-2-methyl-1H-2-benzazepine ***6u***. A mixture of (1′*E*)-2-[2′-(4′′-chlorophenyl)ethenyl]benzaldehyde **1u** (0.65 g, 2.68 mmol) and sarcosine (0.36 g, 4.04 mmol) in dry THF (70 mL) was refluxed for 8 h. The usual work-up as above and chromatography on silica, eluting with petroleum ether 60–80 °C/diethyl ether (80:20) gave 2,3-dihydro-2-methyl-4-(4′-chlorophenyl)-1*H*-2-benzazepine **6u** as a pale yellow oil (0.61 g, 78%); (found: MH^+, 272.101. Calcd for $C_{17}H_{17}N^{37}Cl$: MH, 272.102); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.70 (3H, s, *N*CH_3), 3.85 (2H, s, CH_2), 4.24 (2H, s, CH_2), 5.84 (1H, s, =CH, H-5), 6.94–7.20 (8H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 34.8 (*N*CH_3), 43.5 (CH_2), 54.6 (CH_2), 108.2 (CH), 126.0 (2× CH), 126.4 (CH), 127.82 (CH), 127.88 (CH), 128.0 (2× CH), 129.5 (quat), 130.3 (quat), 135.2 (quat), 137.6 (CH), 140.9 (quat), 143.3 (quat).

3.2.22. 1,4-Diaza-4-methyl-2,6-dioxo-1-phenyl-3-[2′-{2′′-(1′E)-phenylethenyl}phenyl]bicyclo[3.3.0]octane ***12***. A mixture of (1′*E*)-1-formyl-2-(2′-phenylethenyl)benzene **1o** (0.42 g, 2.02 mmol), sarcosine (0.27 g, 3.03 mmol), *N*-phenylmaleimide (0.21 g, 1.2 mmol) and 4 Å molecular sieves (2 g) in anhydrous THF (70 mL) was heated at reflux, under dry nitrogen, for 12 h. After cooling, the solid was removed by filtration and the solvent was evaporated under reduced pressure. Column chromatography of the residue on silica, eluting with petroleum ether 60–80 °C/diethyl ether (90:10 to 70:30), gave 1,4-diaza-4-methyl-2,6-dioxo-1-phenyl-3-[2′-{2′′-(*E*)-phenyethenyl}-phenyl]bicyclo[3.3.0]octane **12** as a white solid (0.27 g, 55%), mp 77–79 °C; (Found: MH^+, 409.192. Calcd for $C_{27}H_{25}N_2O_2$: MH, 409.191); ν_{max} (KBr)/cm^{-1} 1778 (C=O), 1712 (C=O), 1599 (C=C), 1496 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.19 (3H, s, *N*CH_3), 2.68 (1H, m, H-5a), 3.60 (1H, m, H-2a), 3.70 (2H, m, CH_2, H-5), 3.95 (1H, d, *J*=5.9 Hz, H-3), 6.92 (1H, d, *J*=16.2 Hz, =CH), 7.23–7.62 (14H, m, Ar–H), 7.86 (1H, d, *J*=16.2 Hz, =CH); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 39.1 (*N*CH_3), 44.4 (CH_2), 53.9 (CH), 57.8 (CH), 70.5 (CH), 126.45 (2× CH), 126.5 (CH), 126.7 (2× CH), 127.1 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.4 (CH), 128.6 (CH), 128.7 (2× CH), 129.1 (2× CH), 131.5 (CH), 131.7 (quat), 136.3 (quat), 137.5 (quat), 137.7 (quat), 176.3 (C=O), 176.8 (C=O).

3.2.23. 2,3-Dihydro-2-methyl-1H-thieno[2,3-d][2]benzazepine ***6w***. A mixture of 2-(3-thienyl)benzaldehyde **1w** (0.45 g, 2.39 mmol) and sarcosine (0.43 g, 4.83 mmol) in THF (70 mL) was refluxed for 16 h. Chromatography on silica, eluting with hexane/diethyl ether (80 : 20) gave 2,3-dihydro-2-methyl-1*H*-thieno[2,3-*d*][2]benzazepine **6w** as a pale yellow oil (0.35 g, 69%); (found: MH^+, 216.084. Calcd for $C_{13}H_{14}NS$: MH, 216.084); ν_{max} (liquid film)/cm^{-1} 1603 (C=C), 1487 (C=C); ^1H NMR (270 MHz, $CDCl_3$) δ ppm 2.40 (3H, s, *N*CH_3), 3.37 (2H, s, CH_2), 3.57 (2H, s, CH_2), 7.16–7.43 (6H, m, Ar–H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ ppm 43.3 (*N*CH_3), 51.4 (CH_2), 58.2 (CH_2), 123.3 (CH), 126.5 (CH), 126.68 (CH), 126.74 (CH), 127.5 (CH), 130.3 (CH), 134.3 (quat), 135.8 (quat), 137.0 (quat), 140.4 (quat).

3.3. Molecular modelling

Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G*[10,11] level in Gaussian09 software.[12] Reactants and products were fully geometry optimised without symmetry constraints, and characterised as true minima via harmonic frequency calculation. Transition states were then located using quadratic synchronous transit (QST) methods,[13] and characterised by their harmonic frequencies.

Acknowledgements

We thank the EPSRC UK National Mass Spectrometry Facility, Swansea University, U.K. for providing all accurate mass measurements.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.03.078.

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