COMMUNICATION

π-Allyl cation cyclisations initiated by silver(I)-promoted electrocyclic ring opening of ring-fused *gem*-dibromocyclopropanes possessing tethered nucleophiles: the influence of chiral auxiliaries on the diastereoselectivity of cyclisations involving *meso*-substrates

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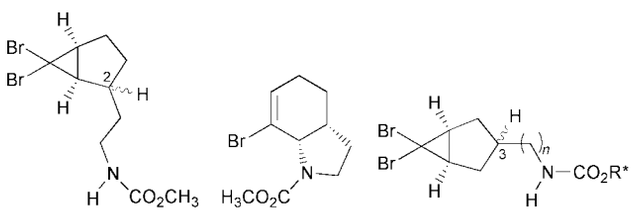
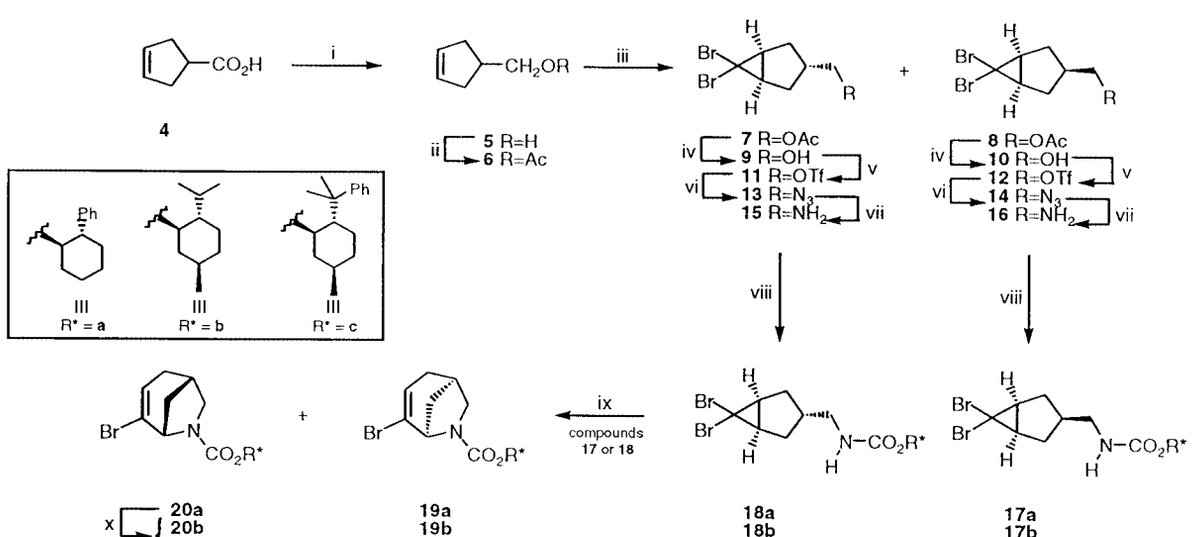
The epimeric pairs of ring-fused *gem*-dibromocyclopropanes 17/18 and 27/28, each of which possesses an internal plane of symmetry and has a tethered carbamate moiety with an associated chiral auxiliary, react with silver perchlorate to give, in a diastereoselective manner, the corresponding pairs of azabicyclic compounds, 19/20 and 29/30 respectively.

Ring-fused *gem*-dibromocyclopropanes are generally easy to prepare (normally *via* addition of dibromocarbene to the corresponding cycloalkene)[1] and often engage in thermal- or silver(I)-promoted electrocyclic ring-cleavage of the three-membered ring[2] to give π-allyl cations. These latter species can be trapped, in an inter- or intra-molecular fashion,[1] by various carbon- and hetero-atom centred nucleophiles.[3,4] The cyclisation reactions associated with the intramolecular trapping processes generate new polycyclic compounds that possess a cycloalkenyl bromide moiety capable of participating in Pd(0)-catalysed cross-coupling reactions. Thus, for example, treatment of either epimer of *gem*-dibromocyclopropane **1** with silver perchlorate results in the smooth and near quantitative formation of the hexahydroindole **2**,[3g] a compound that readily engages in Suzuki cross-couplings[5] with aryl boronic acids. One of the products of such a coupling reaction has been exploited[3g,3h] in a concise synthesis of the alkaloidal degradation product γ-lycorane. On the basis of this and a modest number of additional examples,[3a,3b,3f,4] the title reactions would seem to offer considerable potential in chemical synthesis. At present, however, this type of methodology is under-utilised, perhaps because the basic scope and limitations of such chemistry remain largely undefined. Consequently, we now report that π-allyl cations derived from electrocyclic ring-opening of *meso*-compounds such as 6,6-dibromobicyclo[3.1.0]hexanes possessing a carbamate unit tethered through C-3 (*e.g.* **3**) are subject to diastereoselective ring-closure when the nucleophile has a chiral auxiliary associated with it.[6] The reactions described herein should prove valuable for the synthesis, in enantiopure form, of various azabicyclic species[7] related to bioactive natural products such as epibatidine[8] and anatoxin-a (very fast death factor).[3b,3f,9]



Syntheses of the epimeric forms of *meso*-substrates of the general type **3** ($n = 1$) are shown in Scheme 1. All start with



Scheme 1 *Reagents and conditions* (i) $LiAlH_4$ (0.8 mol equiv.), THF, 66 °C, 6 h ; (ii) Ac_2O (1.9 mol equiv.), pyridine, 18 °C, 16 h; (iii) $CHBr_3$ (excess), C_6H_6, 50% aq. NaOH, TEBAC, 0–18 °C, 42 h; (iv) K_2CO_3 (1.7 mol equiv.), CH_3OH, 18 °C, 8 h; (v) Tf_2O (2.1 mol equiv.), 2,6-lutidine (2.3 mol equiv.), CH_2Cl_2, −60 °C, 0.66 h; (vi) TMGA (3.5 mol equiv.), CH_2Cl_2, −60–18 °C, 6.33 h; (vii) H_2 (excess), 10% Pd on C, THF, 18 °C, 0.5 h; (viii) (−)-menthyl-, (−)-8-phenylmenthyl- or (1*R*)-*trans*-2-phenylcyclohexyl chloroformate (3.33 mol equiv.), Et_3N, THF, 0 °C, 7 h; (ix) $AgClO_4$ (2 mol equiv.), THF, 18 °C, 7 h; (x) $NaOCH_3$ (28 mol equiv.), CH_3OH, 80 °C (sealed tube), 48 h then HCl (gas, excess), 18 °C, 0.1 h then (−)-menthyl chloroformate or (−)-8-phenylmenthyl chloroformate (3 .5 mol equiv.), pyridine, 18 °C, 24 h. TEBAC = triethylbenzylammonium chloride.

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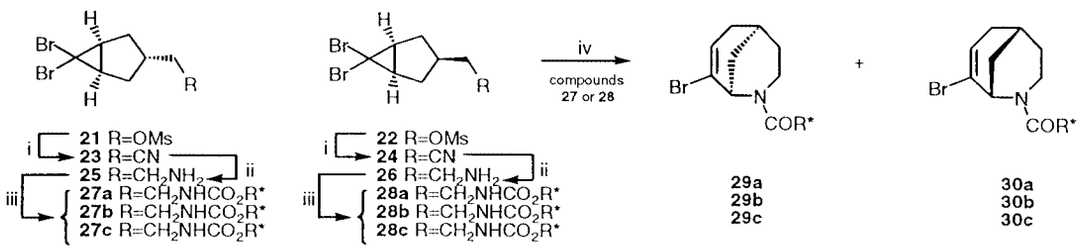
Table 1 Diastereomeric ratios of products obtained from the title cyclisation reactions

Entry	Substrate(s)	Auxiliary (R*)	Ratio of product diastereomers
1	**17a/18a**[a]	(−)-*trans*-2-Phenylcyclohexyl	3:7 (**19a/20a**)
2	**17b/18b**[a]	(−)-Menthyl	2:3 (**19b/20b**)
3	**17c/18c**[a]	(−)-8-Phenylmenthyl	2:9 (**19c/20c**)
4	**27a/28a**[a]	(−)-*trans*-2-Phenylcyclohexyl	5:9 (**29a/30a**)
5	**27b/28b**[b]	(−)-Menthyl	5:6 (**29b/30b**)
6	**27c/28c**[b]	(−)-8-Phenylmenthyl	3:11 (**29c/30c**)

[a] Substrates were subjected to the title reaction either individually or as an epimeric mixture. The product ratios were the same in each case. [b] Substrates were subjected to the title reaction as an epimeric mixture.



Scheme 2 *Reagents and conditions* (i) NaCN (21.5 mol equiv.), DMPU, 18 °C, 68 h; (ii) H_2 (excess), $PtO_2{\cdot}H_2O$, $CHCl_3$, EtOH, 18 °C, 2 h; (iii) (−)-menthyl-, (−)-8-phenylmenthyl- or (−)-(1*R*)-*trans*-2-phenylcyclohexyl chloroformate (*ca*. 2.0 mol equiv.), pyridine, 0–18 °C, 15 h; (iv) $AgClO_4$ (10.0 mol equiv.), DME, 3 Å molecular sieves, 18 °C, 19 h.

conversion of the known acid **4**[10] into the corresponding alcohol **5**[11] (95%), the acetate derivative **6** (97%) of which readily reacts with dibromocarbene generated under Makosza conditions.[1] The resulting *ca*. 2:1 mixture of adducts **7**† and **8** (81% combined yield) was then hydrolysed to the corresponding mixture of alcohols **9** (mp = 46–48 °C) and **10** (95% combined yield). The latter mixture was subjected to reaction with triflic anhydride and the resulting triflates, **11** and **12**, immediately treated with tetramethylguanidinium azide (TMGA)[12] so as to form the corresponding azides, **13** and **14** (86% combined yield) respectively. Reduction of the latter compounds under hydrogenolysis conditions[13] gave a *ca*. 2:1 mixture of amines, **15** and **16**, which reacted with triethylamine and either (−)-menthyl chloroformate (Aldrich), (−)-8-phenylmenthyl chloroformate[14] or (−)-(1*R*)-*trans*-2-phenylcyclohexyl chloroformate[15] to give the corresponding pairs of epimeric carbamates. These could be separated from one another by flash chromatography and in this manner pure samples of compounds **17a** {74% from **16**, $[a]_D = -33$ (*c* 1.8)‡}, **17b** {68% from **16**, mp = 117–118 °C, $[a]_D = -27$ (*c* 1.0)}, **17c** {50% from **16**, $[a]_D = -4$ (*c* 1.7)}, **18a** {74% from **15**, mp = 101–103 °C, $[a]_D = -35$ (*c* 1.0)}, **18b** {68% from **15**, mp = 90–91 °C, $[a]_D = -36$ (*c* 1.4)} and **18c** {50% from (**15**), $[a]_D = -6$ (*c* 1.3)} were obtained. The structure of carbamate **18b** was determined by single-crystal X-ray analysis§ which served to establish the *anti*-relationship between the cyclopropyl and side-chain moieties and, thereby, the structures of all of the related compounds **17a**–**c**, **18a** and **18c**.

Treatment of compound **18a** with silver perchlorate in THF at 18 °C resulted in its smooth conversion into a 3:7 mixture (as determined by GLC analysis) of the diastereoisomeric 6-azabicyclo[3.2.1]oct-3-enes **19a** {26%, $[a]_D = 18$ (*c* 1.6)} and **20a** {60%, mp = 87–88 °C, $[a]_D = -121$ (*c* 1.7)} (Table 1). These products could be separated from one another by flash chromatography and the structure of compound **20a** was established by single-crystal X-ray analysis.§ Reaction of epimer **17a** under analogous conditions gave the same mixture of products in 63% (combined) yield.¶ Related cyclisations were carried out using substrates **17b** and **18b** each of which afforded a separable and *ca*. 2:3 mixture of products **19b** {$[a]_D = 20$ (*c* 0.5)} and **20b** {$[a]_D = -136$ (*c* 0.8)} in 67–73% combined yield. Similarly, each of compounds **17c** and **18c** gave a separable and *ca*. 2:9 mixture of 6-azabicyclo[3.2.1]oct-3-enes **19c** {$[a]_D = 21$ (*c* 0.2)} and **20c** {$[a]_D = -99$ (*c* 1.9)} in 84% combined yield. The structures of compounds **20b** and **20c** were established *via* their independent synthesis from congener **20a**. Thus, carbamate **20a** was hydrolysed to the corresponding amine which was immediately treated with (−)-menthyl chloroformate or (−)-8-phenylmenthyl chloroformate to give authentic samples of compounds **20b** and **20c**, respectively.

The next higher homologues of substrates **17a**–**c** and **18a**–**c**, *viz*. compounds **27a**–**c** and **28a**–**c**, were prepared by the route shown in Scheme 2. Thus, the mixture of mesylates **21** and **22** derived[16] from the corresponding *ca*. 2:1 mixture of alcohols **9** and **10** was converted into the nitriles, **23** and **24** (83% combined yield), by reaction with sodium cyanide in *N*,*N*′-dimethylpropyleneurea (DMPU). Hydrogenation of the latter compounds using PtO_2 as catalyst and in the presence of chloroform afforded the hydrochloride salts of amines **25** and **26** which were immediately treated with pyridine and either (−)-menthyl chloroformate, (−)-8-phenylmenthyl chloroformate or (−)-(1*R*)-*trans*-2-phenylcyclohexyl chloroformate. In this fashion inseparable and *ca*. 2:1 mixtures of carbamates **27b** and **28b** [56% combined yield from precursors **23** and **24**] and compounds **27c** and **28c** (71% combined yield) were obtained. In contrast, congeners **27a** {51% from (**23**), mp = 87–89 °C, $[a]_D = -29$ (*c* 0.8)} and **28a** {51% from (**24**), mp = 108–109 °C, $[a]_D = -32$ (*c* 0.5)} could be separated from one another by HPLC. Reaction of compounds **27a** and **28a**, either independently or as a 2:1 mixture, with silver perchlorate afforded, in 58% combined yield, a *ca*. 5:9 mixture of the 2-azabicyclo[3.3.1]non-7-enes **29a** {$[a]_D = 49$ (*c* 0.5)} and **30a** {$[a]_D = -131$ (*c* 0.6)} (Table 1) which were separated from one another by HPLC. Substrates **27c** and **28c** behaved in a similar manner and afforded, in 33% combined yield, a *ca*. 3:11 mixture of products **29c** {$[a]_D = 110$ (*c* 0.9)} and **30c** {$[a]_D = -108$ (*c* 1.5)}. Reaction of compounds **27b** and **28b** under the same conditions gave, in 54% combined yield, a *ca*. 5:6 mixture of 2-azabicyclo[3.3.1]non-7-enes (**29b**) {mp = 85–87 °C, $[a]_D = 102$ (*c* 0.4)} and **30b** {$[a]_D = -145$ (*c* 0.2)}. Each of the above-mentioned 2-azabicyclo[3.3.1]non-7-enes was accompanied by as yet uncharacterised hydrolysis products. The structure of compound **29b**, the minor cyclisation product derived from precursors **27b** and **28b**, was established by single-crystal X-ray analysis.§ This observation, together with the fact that the specific rotations for all of compounds **20a**–**c** and **30a**–**c** are of the same (negative) sign, effectively implies that the absolute stereochemistries of the azabicyclic ring systems associated with the major cyclisation products are equivalent for the entire series of reactions reported herein.

The origins of the, thus far, modest diastereoselectivities observed in the above-mentioned cyclisation reactions (see Table 1) are the subject of ongoing studies. At this point it

seems reasonable to suggest that since the highest diastereomeric excesses are observed with the 8-phenylmenthyl-based auxiliary,[17] π-stacking effects could be used to advantage in enhancing the selectivities associated with the title processes.

Experimental

Formation of compounds 19c and 20c

A magnetically stirred solution of carbamate **18c** (135 mg, 0.256 mmol) in THF (7.0 ml) maintained under a nitrogen atmosphere at 18 °C was treated, in one portion, with silver perchlorate (104 mg, 0.502 mmol). After 7 h the reaction mixture was filtered through a plug of Celite™ which was washed with dichloromethane (20 ml). The combined filtrates were concentrated under reduced pressure (CAUTION—use a blast shield and do not heat) to give a brown oil which was subjected to flash chromatography (silica gel, 1:7 v/v ethyl acetate–hexane elution). In this manner two fractions, A and B, were obtained.

Concentration of fraction A (R_f 0.4) afforded the 6-azabicyclo[3.2.1]oct-3-ene **19c** (18 mg, 16%) as a clear colourless oil (Found $M^{+\cdot}$, 447.1597. $C_{24}H_{32}{}^{81}BrNO_2$ requires $M^{+\bullet}$, 447.1596). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.19 (complex m, 4H), 7.09 (m, 1H), 5.88 (s) and 5.79 (s) (rotamers,‖ 1H), 4.82 (m, 1H), 4.50 (d, J = 4.8 Hz) and 4.42 (d, J = 4.8 Hz) (rotamers, 1H), 3.17 (d, J = 10.7 Hz) and 2.62 (d, J = 10.7 Hz) (rotamers, 1H), 2.42–2.31 (complex m, 2H), 2.23 (m, 1H), 2.08–1.42 (complex m, 8H), 1.33 (s, 3H), 1.38–1.08 (complex m, 2H), 1.18 (s, 3H), 1.01–0.83 (partially concealed m, 1H), 0.87 (d, J = 6.5 Hz, 3H); ν_{max} (KBr) 2953, 2923, 1697, 1407, 1324, 1234, 1104, 1030, 763 and 700 cm^{-1}; *m/z* 447 (1%) and 445 (1) [$M^{+\bullet}$], 234 (56) and 232 (58), 119 (100) ($C_9H_{11}{}^+$), 118 (75) [$C_9H_{10}{}^{+\bullet}$], 91 (67) ($C_7H_7{}^+$).

Concentration of fraction B (R_f 0.2) afforded the 6-azabicyclo[3.2.1]oct-3-ene **20c** (78 mg, 68%) as a clear colourless oil (Found $M^{+\bullet}$, 447.1596. $C_{24}H_{32}{}^{81}BrNO_2$ requires $M^{+\bullet}$, 447.1596). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.23 (complex m, 4H), 7.11 (m, 1H), 5.86 (broad s) and 5.72 (broad s) (rotamers, 1H), 4.78 (dt, J = 10.6 and 4.3 Hz) and 4.71 (dt, J = 10.7 and 4.3 Hz) (rotamers, 1H), 4.44 (d, J = 4.4 Hz) and 2.94 (d, J = 4.4 Hz) (rotamers, 1H), 3.43 (ddd, J = 10.7, 5.9 and 1.9 Hz, 1H), 3.09 (d, J = 11.0 Hz, 1H), 2.48 (m, 1H), 2.35 (dm, J = 18.1 Hz, 1H), 2.18–1.79 (complex m, 6H), 1.70–1.57 (complex m, 2H), 1.47 (broad m, 1H), 1.36 (s) and 1.33 (s) (rotamers, 3H), 1.18 (s, 3H), 1.14 (m, 1H), 0.94 (m, 1H), 0.88 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0 and 152.9 (rotamers, C), 127.8 (CH), 127.1 (CH), 125.2 (CH), 124.4 (CH), 123.2 and 123.0 (rotamers, C), 75.0 and 74.5 (rotamers, CH), 59.9 and 58.8 (rotamers, CH), 52.5 and 50.8 (rotamers, CH_2), 50.8 and 50.6 (rotamers, CH), 42.6 and 41.9 (rotamers, C), 39.4 (CH_2), 36.2 (CH_2), 35.8 and 35.6 (rotamers, CH_2), 35.0 and 34.7 (rotamers, CH_2), 31.7 and 31.3 (rotamers, CH or CH_3), 30.8 (CH or CH_3), 29.7 (CH or CH_3), 26.4 (CH_2), 23.1 (CH or CH_3), 21.9 (CH_3), one signal due to a low field quaternary carbon not observed; ν_{max} (KBr) 2954, 2924, 1693, 1415, 1329, 1274, 1108, 788 and 763 cm^{-1}; *m/z* 447 (3%) and 445 (3) [$M^{+\bullet}$], 234 (70) and 232 (72), 119 (100) ($C_9H_{11}{}^+$), 118 (87) [$C_9H_{10}{}^{+\bullet}$], 105 (52), 91 (69) ($C_7H_7{}^+$).

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Notes and references

† All new and stable compounds had spectroscopic data [IR, UV, NMR, mass spectrum] consistent with the assigned structure. Satisfactory combustion and/or high-resolution mass spectral analytical data were obtained for new compounds and/or suitable derivatives.

‡ All optical rotations were determined in chloroform solution at 20 °C and are given in 10^{-1} deg cm^2 g^{-1}. Concentrations (*c*) are given in g 100 ml^{-1}.

§ *Crystal data* for compound **18b**: $C_{18}H_{29}Br_2NO_2$, M = 451.24, T = 193 K, orthorhombic, space group $P2_12_12_1$ (#19), Z = 4, a = 7.080(3), b = 9.637(1), c = 29.064(2) Å, U = 1982.9(9) Å^3, μ(Cu-Kα) = 52.94 cm^{-1}, 1730 unique data ($2\Theta_{max}$ = 119.9°), 1605 with $I > 3\sigma(I)$; R = 0.033, R_w = 0.041, S = 2.56.

Crystal data for compound **20a**: $C_{20}H_{24}BrNO_2$, M = 390.32, T = 193 K, orthorhombic, space group $P2_12_12_1$ (#19), Z = 4, a = 9.591(2), b = 12.8947(9), c = 14.871(2) Å, U = 1839.2(4) Å^3, μ(Cu-Kα) = 31.38 cm^{-1}, 5862 reflections measured, 2738 unique (R_{int} = 0.037, $2\Theta_{max}$ = 120.1°), 2682 with $I > 2\sigma(I)$; R = 0.020, R_w = 0.026, S = 1.17.

Crystal data for compound **29b**: $C_{19}H_{30}BrNO_2$, M = 384.36, T = 200(1) K, monoclinic, space group $P2_1$, Z = 2, a = 8.4008(5), b = 9.9077(6), c = 11.8739(8) Å, β = 97.278(4)°, U = 980.3(5) Å^3, μ(Mo-Kα) = 21.1 cm^{-1}, 9089 reflections measured, 3263 unique (R_{int} = 0.048, $2\Theta_{max}$ = 25.0°), 2453 with $I > 3\sigma(I)$; R = 0.042, R_w = 0.045, S = 1.18.

The structures of **18b** and **20a** were refined by full-matrix least squares analysis on F using the teXsan structure analysis software of Molecular Structure Corporation.[18] Data for compound **29b** were extracted using the DENZO package.[19] Structure solution was by direct methods (SIR92)[20] and refinement was by full matrix least-squares on F using the maXus program package.[21] CCDC reference number 207/442. See http://www.rsc.org/suppdata/p1/b0/b002525i/ for crystallographic files in .cif format.

¶ These observations indicate that the cyclisation process is insensitive to the stereochemical relationship between the tethered nucleophile and cyclopropyl moiety. In our view, such observations also suggest the intermediacy of a discrete and common π-allyl cation.

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