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Amidines as potent nucleophilic organocatalysts for the transfer of electrophilic bromine from *N*-bromosuccinimide to alkenes

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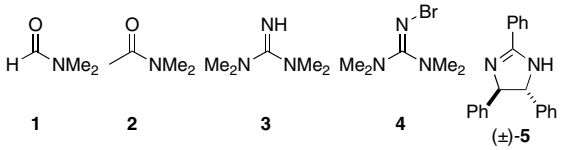
Abstract—(±)-*iso*-Amarine is a potent organocatalyst at 1 mol % loading for both the bromoacetoxylation of alkenes with added acetic acid and bromolactonisation of unsaturated carboxylic acids with stoichiometric NBS as the electrophilic bromine source. A simple bromoamidine with an N–Br bond has been characterised crystallographically for the first time. Asymmetric induction in the bromination reactions with enantiopure amidines was zero.

The electrophilic bromination of alkenes via a bromonium ion is a fundamental transformation in organic chemistry.[1] When the bromonium ion is not to be opened by a bromide anion, the archetypal reagent for this purpose is *N*-bromosuccinimide (NBS) where it has enjoyed widespread use as a stoichiometric reagent in the bromohydration, bromoetherification and bromolactonisation reactions of alkenes.[2] We have recently reported that dimethyl formamide **1** (DMF), dimethylacetamide **2** (DMA) and tetramethylguanidine **3** (TMG) act as nucleophilic organocatalysts for the transfer of electrophilic bromine from NBS to alkenes as exemplified by bromolactonisations of γ,δ and δ,ε-unsaturated carboxylic acids (DMF, DMA and TMG) and for the intermolecular bromoacetoxylation of alkenes (TMG).[3] In that report, we speculated that the de facto active brominating species when using TMG as the catalyst was (protonated) *N*-bromoguanidine **4**, and noted that 2-bromotetramethylguanidine has been reported by the direct halogenation of 1,1,3,3-tetramethylguanidine.[4] In our continued efforts in this area[5] we now report that amidines are also potent catalysts for the transfer of electrophilic bromine from NBS to alkenes. Further, we present the first simple *N*-bromoamidine to be characterised by X-ray crystallography, unambiguously confirming the presence of an N–Br bond, and show that it is an intermediate in the catalytic cycle for the electrophilic bromine transfer to alkenes. We also report on the ability of enantiopure amidines to transfer electrophilic bromine to alkenes in an asymmetric fashion.



1 **2** **3** **4** (±)-**5**

We selected readily available (±)-*iso*-amarine **5**[6] as a representative amidine to test as a catalyst (Table 1). It proved to be an excellent catalyst at just 1 mol % loading for both bromoacetoxylation of alkenes **6**–**9** with added acetic acid (entries 2–5) and bromolactonisation of unsaturated carboxylic acids **10**–**12** (entries 6–8) with stoichiometric NBS as the electrophilic bromine source

Keywords: Electrophilic bromination; Alkenes; Organocatalysis; Amidine.
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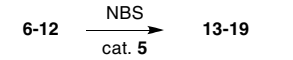
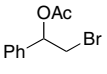
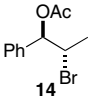
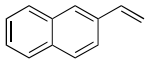
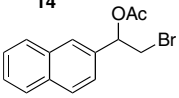
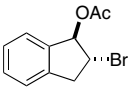
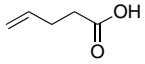
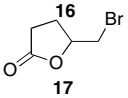
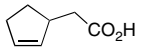
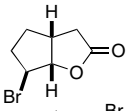
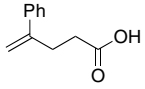
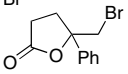
Table 1. Bromoacetoxylation and bromolactonisation using catalyst (±)-**5**[a]



Entry	Substrate[b]	Catalyst loading (mol %)	AcOH (equiv)	Time (h)	Product[c]	Conversion[d] (%)
1	 **6**	10	4	0.5	 **13**	100
2	**6**	1	4	2	**13**	95
3	 **7**	1	4	1	 **14**	91[e]
4	 **8**	1	4	1	 **15**	96
5	 **9**	1	4	0.5		93[f]
6	 **10**	1	0	1	 **17**	90[g]
7	 **11**	1	0	1		86[g]
8	 **12**	1	0	1	 **19**	86[g]

[a] All reactions were performed with 1.0 equiv of NBS at rt in $CDCl_3$ (entries 1–5) or CH_2Cl_2 (entries 6–8) at 0.25 M concentration.
[b] The substrates **6**–**11** are all commercially available compounds. For details on the preparation of carboxylic acid **12** see Ref. 5.
[c] The products are all known compounds. For full characterisation data on bromoacetates **13**–**14** see Ref. 3. For characterisation data on compounds **15**–**16** see footnote †. For full characterisation data on bromolactone adducts **17**–**19** see Ref. 5.
[d] As determined by ^{1}H NMR.
[e] As an 85:15 mixture of diastereoisomers (major isomer shown).
[f] As a 9:1 mixture of diastereoisomers (major isomer shown).
[g] Isolated yield after work-up.

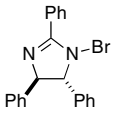
giving products **13**–**19**.† Its activity is up to an order of magnitude superior to that previously reported for TMG **3**.[3] The bromoacetoxylation products display excellent regiocontrol for attack of acetic acid at the benzylic position of the bromonium ion (entries 1–5), as expected, with the presence of minor diastereoisomers (entries 3 and 5) arising from intervention of a free benzylic carbocation.[7] In all cases the corresponding control experiment without added catalyst gave <5% conversion to the brominated product over the same time period.

Previously we suggested that (protonated) *N*-bromoguanidine **4** was the key intermediate in a catalytic cycle using TMG **3** as a catalyst.[3] We now propose that (protonated) bromoamidine **20** is the analogous intermediate when using (±)-*iso*-amarine **5** as the catalyst. *N*-Bromoamidines are known in the literature,[8] but attempts to isolate **20** by the stoichiometric reaction of amidine **5** with NBS led only to extensive decomposition.‡ In

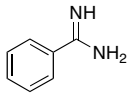
† Data for products **15**–**16**. *(±)-1-Naphthyl-1-acetoxy-2-bromoethane* (**15**): Colourless oil; $R_f = 0.30$ (50:50 CH_2Cl_2: 40–60 °C petroleum ether); IR (thin film) υ_{max} 1742 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.90–7.80 (m, 4H, Ar*H*), 7.54–7.43 (m, 3H, Ar*H*), 6.16 (dd, $J = 7.8$, 4.8 Hz, 1H, C*H*OAc), 3.79–3.63 (m, 2H, CH_2Br), 2.17 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 170.0, 135.1, 133.5, 133.1, 128.8, 128.2, 127.9, 126.7, 126.6, 126.3, 123.9, 75.1, 34.3, 21.1; MS (C.I.) *m/z* 312, 310 $[M+NH_4]^+$, 292, 294, $[M+H]^+$; HRMS calcd for $[M+NH_4]^+$ $C_{14}H_{17}O_2N^{81}Br$: 312.0422. Found: 312.0414; HRMS calcd for $[M+NH_4]^+$ $C_{14}H_{17}O_2N^{79}Br$: 310.0443. Found: 310.0444. *(±)-Indeneacetoxybromide* (**16**): Colourless oil; $R_f = 0.31$ (50:50 CH_2Cl_2: 40–60 °C petroleum ether.); IR (thin film) υ_{max} 1737 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) major isomer only; δ 7.43–7.20 (m, 4H, Ar*H*), 6.32 (d, $J = 3.5$ Hz, 1H, C*H*O), 4.52–4.47 (m, 1H, C*H*Br), 3.70 (dd, 1H, $J = 6.7$, 17.0 Hz, CH*H*), 3.26 (dd, 1H, $J = 4.2$, 17.0 Hz, C*H*H), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) major isomer only; δ 170.4, 141.3, 138.6, 129.8, 127.7, 126.0, 124.9, 84.0, 50.0, 41.5, 21.1; MS (E.I.) *m/z* 255, 253 $[M]^+$; HRMS (C.I,) calcd for $[M+NH_4]^+$ $C_{11}H_{15}NO_2{}^{81}Br$: 274.0266. Found: 274.0267; HRMS calcd for $[M+NH_4]^+$ $C_{11}H_{15}$ $NO_2{}^{81}Br$ 272.0286. Found: 272.0286.

‡ The reaction of *iso*-amarine **5** with NBS in $CDCl_3$ generated a yellow-green solution. ^{1}H NMR analysis after 15 min revealed that all the NBS had been consumed with the characteristic peak for succinimide appearing at 2.75 ppm. The ^{13}C NMR showed that the N–*C*=N resonance of **5** at 163.2 ppm had completely disappeared and considerable line broadening of the resonance at 143.6 ppm had occurred. However, attempts to isolate any new species led to decomposition.

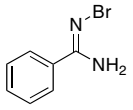
contrast, the stoichiometric reaction of benzamidine **21** with NBS in carbon tetrachloride gave *N*-bromoamidine **22**[9,§] as yellow needles suitable for X-ray crystallography (Fig. 1). The solid state structure revealed the presence of two crystallographically independent molecules **A** and **B** (molecule **A** is shown in Fig. 1, and molecule **B** in Fig. S1 in the electronic Supplementary data). The two N–Br bond lengths [1.9002(18) Å in molecule **A**, and 1.9087(18) Å in molecule **B**] are slightly longer than those seen in other literature species with C=N–Br moieties, though there are so few that the comparisons must be made with caution.[10] This is the first time that a *N*-bromoamidine has been characterised crystallographically.[¶]



20



21



22

Isolated, pure *N*-bromoamidine **22** (1.0 equiv) proved to act as a stoichiometric electrophilic bromine donor when allowed to react with *trans*-anethole **23** (1.0 equiv) and acetic acid (4.0 equiv) giving 50% conversion to bromoacetate **24**[‖] in 10 min, with benzamidine **21** as the only other detectable product. Benzamidine **21** itself was found to act as a catalyst (10 mol %) for the same bromination reaction with stoichiometric NBS (1.0 equiv) with quantitative conversion to **24** after 3 h.

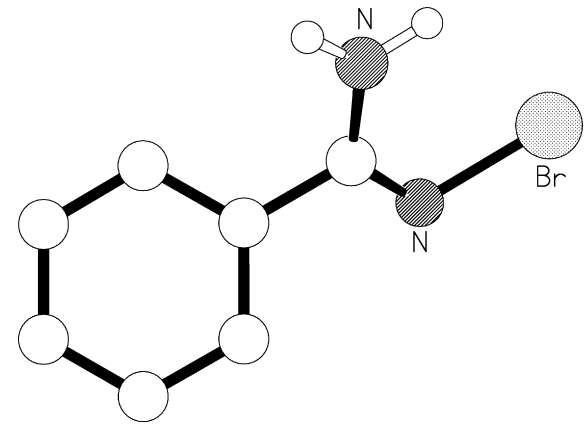
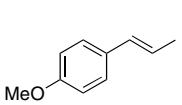
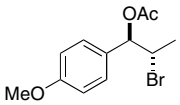


Figure 1. The molecular structure of one (**A**) of the two crystallographically independent molecules present in the crystals of **22**.

When a catalytic quantity (10 mol %) of *N*-bromoamidine **22** was added instead, a quantitative conversion to brominated product **24** was also obtained after 3 h. These experiments demonstrate conclusively that (protonated) *N*-bromoamidine **22** is an intermediate in the catalytic cycle (Scheme 1).



23



24

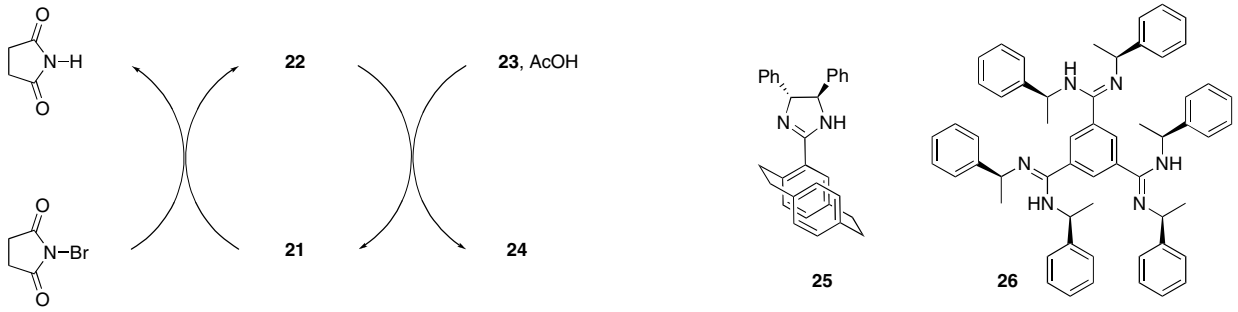
Having defined the nature of the catalytic intermediate, the possibility of performing asymmetric bromoacetoxylation or bromolactonisation using a chiral amidine was explored. Enantiopure (*R*,*R*)-*iso*-amarine **5**,[11] novel planar-chiral [2.2]paracyclophane amidine **25** and novel C_3-symmetric amidine **26** were selected as potential asymmetric catalysts. Amidine **25** was prepared from the known (*S*)-4-carboxamido[2.2]paracyclophane[12] via imidate formation followed by treatment with commercially available (*R*,*R*)-1,2-diamino-1,2-diphenylethane.[††] The C_3-symmetric amidine **26** was prepared by the

[§] Benzamidine **21** (622 mg, 5.2 mmol) was mixed with NBS (920 mg, 5.2 mmol) in CCl_4 (15 mL), stirred for 1 h and the reaction mixture cooled to −5 °C. The precipitate was filtered off and the filtrate evaporated to give a crude solid. Recrystallisation yielded the *N*-bromoamidine **22** (522 mg, 50%) as yellow needles; mp 73–74 °C (1-chlorobutane/40–60 °C petroleum ether) [lit.[9] 81 °C]; IR (KBr disc cm^{-1}) υ_{max} 3399, 3278, 3148, 1624 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.59 (m, 2H, Ar*H*), 7.45–7.39 (m, 3H, Ar*H*), 5.67 (br s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 164.7, 132.4, 131.1, 128.8, 127.0; MS (E.I.) *m*/*z* 200, 198 $[M]^+$; HRMS calcd for $[M]^+$ $C_7H_7N_2{}^{81}Br$: 199.9772. Found 199.9773; HRMS calcd for $[M]^+$ $C_7H_7N_2{}^{79}Br$: 197.9793. Found: 197.9792; Anal. Calcd for $C_7H_7N_2Br$: C, 42.24; H, 3.54; N, 14.07. Found: C, 42.22; H, 3.45; N, 13.95. *Crystal data for* **22**: $C_7H_7BrN_2$, $M = 199.06$, monoclinic, $P2_1/c$ (no. 14), $a = 7.7873(4)$, $b = 16.1058(8)$, $c = 12.3914(6)$ Å, $\beta = 92.032(4)°$, $V = 1553.16(13)$ Å^3, $Z = 8$ (2 independent molecules), $D_c = 1.703$ g cm^{-3}, μ(Mo-Kα) = 5.215 mm^{-1}, $T = 173$ K, colourless platy needles, Oxford Diffraction Xcalibur 3 diffractometer; 5329 independent measured reflections, F^2 refinement, $R_1 = 0.037$, $wR_2 = 0.076$, 3692 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{max} = 65°$], 197 parameters. CCDC 644181.

[¶] A search of the Cambridge Structural Database (version 5.28, Jan-07 update) failed to find any such structures. For a crystalline bromoamidine, that is, also part of a heterocyclic system, see Ref. 10b.

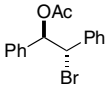
[‖] Data for **24**: Colourless oil; $R_f = 0.23$ (50:50 CH_2Cl_2/40–60 °C petroleum ether); IR (thin film) υ_{max} 1744 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.31 (d, $J = 7.5$ Hz, 2H, Ar*H*), 6.91 (d, $J = 7.5$ Hz, 2H, Ar*H*), 5.90 (d, $J = 5.2$ Hz, 1H, C*H*O), 4.36 (dq, $J = 6.8$, 5.2 Hz, 1H, C*H*Br), 3.83 (s, 3H, OCH_3), 2.16 (s, 3H, O_2CCH_3), 1.67 (d, $J = 6.8$ Hz, 3H, CHBrCH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 169.7, 159.7, 129.3, 128.6, 113.8, 78.0, 55.3, 50.6, 21.1, 21.1; MS (C.I.) *m*/*z* 306, 304 $[M+NH_4]^+$; HRMS calcd for $[M+NH_4]^+$ $C_{12}H_{19}NO_3{}^{81}Br$ 306.0528. Found: 306.0527; HRMS calcd for $[M+NH_4]^+$ $C_{12}H_{19}NO_3{}^{79}Br$ 304.0548. Found: 304.0547.

[††] A solution of triethyloxonium tetrafluoroborate (0.8 mL, 1 M, 0.8 mmol) in CH_2Cl_2 was added to a suspension of (*S*)-4-carboxamido[2.2]paracyclophane (190 mg, 0.8 mmol) in CH_2Cl_2 and the mixture stirred for 14 h. Dry EtOH (2 mL) was added, the reaction stirred for 5 min and (*R*,*R*)-1,2-diamino-1,2-diphenylethane (175 mg, 0.8 mmol) added. The reaction was stirred for a further 14 h, diluted with CH_2Cl_2 (100 mL) and washed with aqueous NaOH solution (75 mL, 5% w/v). The organic phase was dried ($MgSO_4$) and evaporated to give the crude amidine. Column chromatography yielded the amidine **25** (100 mg, 30%) as a colourless oil; $R_f = 0.25$–0.50 (50:50 EtOAc:40–60 °C petroleum ether); $[\alpha]_D^{25}$ +42.0 (*c* 0.1, CH_2Cl_2); IR (thin film) υ_{max} 3385, 3029, 2927, 2856 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.41–7.28 (m, 10H, Ar*H*), 7.01 (d, $J = 1.6$ Hz, 1H, H5), 6.83 (d, $J = 7.8$ Hz, 1H, H7), 6.60–6.50 (m, 5H, Ar*H*), 5.05 (s, 1H, N*H*), 4.02 (m, 1H, H2′), 3.25–2.90 (m, 9H, ArCH_2, PhC*H*C*H*Ph); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 163.7, 144.1, 140.2, 139.7, 139.4, 136.1, 134.7, 132.9, 132.8, 132.7, 131.7, 130.8, 128.8, 127.6, 126.7, 60.0, 35.4, 35.3, 35.2, 31.0; MS (E.I.) *m*/*z* 428 $[M]^+$; HRMS calcd for $[M]^+$ $C_{31}H_{28}N_2$ 428.2244. Found: 428.2248. Anal. Calcd for $C_{31}H_{28}N_2$: C, 86.88; H, 6.59; N, 6.54. Found: C, 86.79; H, 6.56; N, 6.61.



Scheme 1. The catalytic cycle with bromoamidine **22**.

Table 2. Attempted asymmetric bromoacetoxylation and bromolactonisation using catalysts (*R*,*R*)-**5**, **25** and **26**[a]

Entry	Catalyst	Catalyst loading (mol %)	Substrate	Time (h)	Temperature (°C)	Product	Yield[b] (%)	ee[c] (%)
1	**5**	1	**11**	8	−78	**18**	50	0
2	**5**	1	**10**	1.5	rt	**17**	92	0
3[d]	**26**	5		18	−20		40	0
4	**25**	5	**7**	28	−78	**14**	5	Nd
5	**26**	5	**7**	28	−78	**14**	45	0
6	**25**	5	**23**	21	−78	**24**	50	0
7	**26**	5	**23**	21	−78	**24**	53	0

[a] All reactions were performed with 1.0 equiv of NBS in $CHCl_3$ (entries 1–3) or CH_2Cl_2 (entries 4–8) at 0.25 M concentration.
[b] Isolated yield after chromatography.
[c] Determined by chiral HPLC.
[d] For characterisation data for this product see Ref. 3.

conversion of known homochiral *N*,*N*′,*N*″-tris(1-phenylethyl)-1,3,5-benzenetricarboxamide[13] into its tris imidoyl chloride followed by immediate treatment with (*S*)-α-methylbenzylamine.[‡‡] However, for all the bromination reactions surveyed, under all conditions, no asymmetric induction was observed (Table 2).

In conclusion, we have shown that amidines act as potent nucleophilic organocatalysts for the transfer of electrophilic bromine from NBS to alkenes, and have characterised an *N*-bromoamidine intermediate on the catalytic cycle. Our preliminary results with enantiopure amidine catalysts show that the catalytic asymmetric bromination of prochiral alkenes via an asymmetric bromonium ion remains an extremely challenging and currently unsolved problem.[14]

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.112.

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[‡‡] A mixture of *N*,*N*′,*N*″-tris(1-phenylethyl)-1,3,5-benzenetricarboxamide (1.5 g, 2.8 mmol) and PCl_5 (2.08, 10.1 mmol) in PhMe (30 mL) was heated to reflux for 5 min until all solids had entered solution. The solution was immediately cooled to −10 °C and filtered. The solution was then re-cooled under an inert atmosphere of nitrogen to −10 °C and (*S*)-α-methylbenzylamine (2.2 mL, 17 mmol) was added dropwise over 5 min. The reaction was allowed to reach rt over 3 h, stirred for a further 14 h, then refluxed for 5 h. The resulting mixture was cooled to rt, evaporated to dryness, dissolved in CH_2Cl_2 (100 mL) and washed with aqueous NaOH solution (5% w/v, 100 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL) and the organics combined, dried ($MgSO_4$) and evaporated to give the crude product as a white solid (2.5 g). Portions of the crude mixture (30 mg) were purified via preparative TLC on alumina giving the pure tris-amidine **26** as a colourless oil (15 mg, 70%): $R_f = 0.50–0.65$ (20:80 Et_3N:PhMe); IR (KBr plate, cm^{-1}) 3417, 3060, 3026, 2968, 2925, 1639, 1491, 1449; $[\alpha]_D^{25}$ −37.0 (*c* 0.3, CH_2Cl_2); ^1H NMR ($CDCl_3$, 270 MHz) δ 7.4–6.8 (br m, 36 H, Ar*H*, N*H*), 1.50–1.15 (br m, 24 H, C*H*$_3$); ^{13}C NMR (DMSO, 68 MHz) δ 147.5 (br), 130.5, 129.6, 128.9, 128.1 (br), 25.8 (br); MS (FAB) *m*/*z* 829 $[M+H]^+$, 724, 355, 281, 221, 207, 147; HRMS calcd for $[M+H]^+$ $C_{57}H_{61}N_6$: 829.4958. Found: 829.4974.

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