(10% ether in petroleum ether), 1.01 g (79%) of **24** as a colorless solid, mp 126.5–128 °C: ^{1}H NMR δ 7.38 (t, 1 H, J = 7.5 Hz), 7.46 (t, 2 H, J = 7.5 Hz), 7.55 (t, 2 H, J = 7.5 Hz), 7.67 (t, 1 H, J = 7.5 Hz), 7.84 (d, 2 H, J = 7.5 Hz), 8.15 (s, 1 H), 8.59 (d, 2 H, J = 7.5 Hz); ^{13}C NMR δ 125.84, 128.48, 128.84, 128.90, 129.93, 131.03, 134.02, 134.96, 136.22, 142.70, 157.55, 178.70; IR (KBr) 3140 (w), 1660 (s), 1600 (m), 1520 (m), 1480 (s), 1450 (m), 1350 (s), 1280 (s), 1170 (s), 1130 (s), 970 (m), 940 (m), 910 (s) cm^{-1}; MS 250 (3), 249 (P, 18), 105 (100), 77 (42), 51 (13); HRMS calcd for $C_{16}H_{11}NO_2$ 249.0790, found 249.0765.

2-Ethoxy-4,5-diphenyloxazole (26). The method of Dziomko and Ivashchenko[24] was used to convert benzoin to 4,5-diphenyl-2(3*H*)-oxazolone (**25**), in 52% yield, mp 208–210 °C (lit.[17] mp 211 °C): ^{1}H NMR δ 7.29–7.34 (m, 3 H), 7.40–7.45 (m, 3 H), 7.50–7.53 (m, 4 H), 10.16 (s, 1 H).

A slurry of **25** (2.235 g, 9.42 mmol) in 15 mL of CH_2Cl_2 was treated with triethyloxonium tetrafluoroborate (3.58 g, 18.8 mmol) in 10 mL of CH_2Cl_2, and the mixture was stirred overnight, effecting conversion to a clear pale yellow solution. The pH was brought to ca. 9 by dropwise addition of 3 M KOH (ca. 14 mL), with stirring continued for an additional 15 min. This mixture was added to 100 mL of water and extracted with CH_2Cl_2 (3 × 50 mL). Washed with brine, dried over K_2CO_3, and evaporated, the crude product was obtained as a yellow oil (2.52 g). Silica gel chromatography (10% ether in petroleum ether, R_f = 0.23) returned 2.43 g (97%) of **26** as a colorless solid, mp 61–62.5 °C (lit.[17] mp 64–66 °C): ^{1}H NMR δ 1.48 (t, 3 H, J = 7 Hz), 4.54 (q, 2 H, J = 7 Hz), 7.25 (t, 1 H, J = 7.5 Hz), 7.31 (t, 3 H, J = 7.5 Hz), 7.36 (t, 2 H, J = 7.5 Hz), 7.52 (d, 2 H, J = 7.5 Hz), 7.63 (d, 2 H, J = 7.5 Hz).

2-Ethoxy-4,5-dimethyloxazole (27). Following the general procedure from the literature,[24] we heated a mixture of commercial acetoin (4.41 g, 50 mmol), KOCN (4.46 g, 55 mmol), and DMF (15 mL) to 120 °C, at which point a solution of concd HCL (6 mL) in DMF (10 mL) was slowly added. The internal temperature was increased to 135 °C, and this was maintained for 2 h. After brief cooling, the mixture was poured into water, extracted with CH_2Cl_2 (4 × 40 mL), and worked up in the usual manner. The residue in CH_2Cl_2 was passed through a short plug of silica gel to give 4.1 g of a light brown solid. This was taken up in CH_2Cl_2 and treated with triethyloxonium tetrafluoroborate followed by base as described above. The brown oil that resulted was chromatographed (20% ether in petroleum ether) to give 569 mg (8% based on acetoin) of this unknown oxazole as a colorless liquid: ^{1}H NMR δ 1.40 (t, 3 H, J = 7 Hz), 1.98 (s, 3 H), 2.12 (s, 3 H), 4.36 (q, 2 H, J = 7 Hz); ^{13}C NMR δ 9.36, 11.08, 14.13, 66.36, 128.59, 137.04, 159.62; IR (neat) 2995 (m), 2945 (m), 1600 (s), 1445 (m), 1380 (s), 1350 (s), 1320 (m), 1240 (s), 1140 (m), 1075 (m), 1030 (m) cm^{-1}; MS 142 (6), 141 (64), 114 (8), 113 (100), 112 (29), 84 (16), 69 (11), 43 (57); HRMS calcd for $C_7H_{11}NO_2$ 141.0790, found 141.0768.

Acnowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **5a,b**, **6**, **9–11**, **13**, **15**, **19**, **20**, **22**, **24**, and **27** (26 pages). Ordering information is given on any current masthead page.

(24) Dziomko, V. M.; Ivashchenko, A. V. *Zh. Org. Khim.* **1973**, *9*, 2191 (Engl. transl., p 2206).

(25) **Note added in proof:** A recent paper describes additional unusual reactions of lithiooxazoles: Hodges, J. C.; Patt, W. C.; Connolly, C. J. *J. Org. Chem.* **1991**, *56*, 449.

Electroorganic Chemistry. 129. Electroreductive Synthesis of Chiral Piperazines and Enantioselective Addition of Diethylzinc to Aldehydes in the Presence of the Chiral Piperazines

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Electroreduction of diimines, prepared from 1,2-diamines and aromatic aldehydes, in acidic media gave intramolecularly coupled products, 2,3-diarylpiperazines, stereoselectively. Chiral tri- and tetrasubstituted piperazines were synthesized effectively from chiral 1,2-diamines by the same electroreductive method. Chiral piperazines, prepared from 1(*R*),2(*R*)-diaminocyclohexane were effective chiral ligands of catalysts for the enantioselective addition of diethylzinc to aldehydes.

Chiral 1,2-diamines have been known to be effective ligands of catalysts for enantioselective synthesis of some chiral compounds.[1] The methods of synthesis of chiral 1,2-diamines were, however, rather limited. Reductive intermolecular coupling of imines promoted by metal reducing agents has been reported as one of the methods,[2] though complete stereoselectivity was not always achievable.

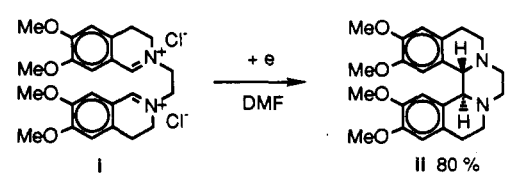
On the other hand, chiral piperazines also seem to be effective chiral ligands. The electroreduction of *N,N'*-dibenzylideneethylenediamine leading to the formation of *trans*-2,3-diphenylpiperazine **1** (R^1 = R^2 = H, 42% yield),[3,4]

(1) For recent studies on the enantioselective synthesis using chiral 1,2-diamine derivatives see: (a) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. (b) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *Ibid.* **1989**, *111*, 5493. (c) Corey, E. J.; Yu, C.-M.; Kim, S. S. *Ibid.* **1989**, *111*, 5495. (d) Corey, E. J.; Yu, C.-M.; Lee, D.-H. *Ibid.* **1990**, *112*, 878.

(2) (a) Smith, J. G. *Can. J. Chem.* **1966**, *44*, 59. (b) Smith, J. G.; Veach, C. D. *Ibid.* **1966**, *44*, 2497. (c) Smith, J. G.; Ho, I. J. *J. Org. Chem.* **1972**, *37*, 653. (d) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152. (e) Mangeneg, P.; Tejero, T.; Alexakis, A.; Grosjean, F.; Normant, J. *Synthesis* **1988**, 255. (f) Betschart, C.; Schmidt, B.; Seebach, D. *Helv. Chim. Acta* **1988**, *71*, 1999.

(3) Koch, R. W.; Dessy, R. E. *J. Org. Chem.* **1982**, *47*, 4452.

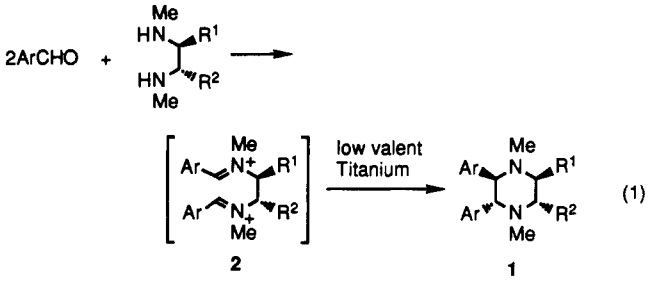
(4) We have also found that the electroreduction of diisiquinolinium salt **i** gave the corresponding coupled product **ii** stereoselectively.[5]



I **II** 80 %

0022-3263/91/1956-3063$02.50/0

for instance, has been reported to be a typical stereoselective method for synthesis of 2,3-diphenylpiperazine. Recently, it was also reported that reductive intramolecular coupling of diiminium salts **2** using low-valent titanium as the reducing agent gave *N,N'*-dimethyl-2,3-diarylpiperazines **1** stereoselectively (eq 1; $R^1 = R^2 = H$, 42%;

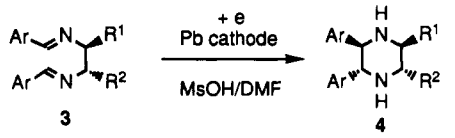


(1)

2 **1**

R^1 = alkyl, $R^2 = H$, 7–30%; $R^1 = R^2 = -(CH_2)_4-$, 8–19%).[2f] Chiral piperazines were obtained by using chiral 1,2-diamines as the starting materials. In these two types of methods, however, the yields of **1** were unsatisfactory and the piperazines obtained by these methods were limited to *N,N'*-dimethylated piperazines. N,N'-Unsubstituted piperazines seem to be more useful materials for the creation of chiral catalysts than N,N'-dimethylated compounds, since the former are able to be easily modified by introducing appropriate substituents on the nitrogen atoms. The stereoselective synthesis of chiral N,N'-unsubstituted piperazines is, however, hitherto unknown.

In this paper, the electroreductive intramolecular coupling of aromatic diimines **3** was found to be an effective method leading to the formation of N,N'-unsubstituted 2,3-diarylpiperazines **4** (eq 2). This method was re-



(2)

3 **4**

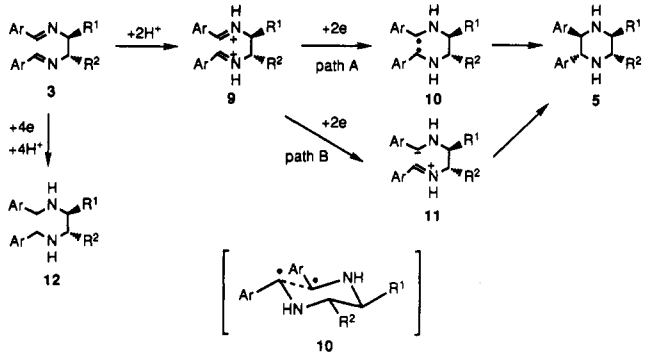
markably effective for the stereoselective synthesis of chiral tri- and tetrasubstituted piperazines. It was also found that chiral piperazines derived from **4** were effective ligands of catalysts for the enantioselective addition of diethylzinc to aldehydes.

Table I. Electroreductive Intramolecular Coupling of 3 to 4

run		Ar	R^1	R^2		% yield[a]
1	**3a**	C_6H_5	H	H	**4a**	95
2	**3b**	*p*-$MeOC_6H_4$	H	H	**4b**	82
3	**3c**	*m*-$BnOC_6H_4$	H	H	**4c**	80
4	**3d**	*p*-ClC_6H_4	H	H	**4d**	75
5	**3e**	*o*-HOC_6H_4	H	H	**4e**	42
6	**3f**	*p*-$MeO_2CC_6H_4$	H	H	**4f**	50
7	**3g**	1-naphthyl	H	H	**4g**	62
8	**3h**	C_6H_5	Me[b]	H	**4h**	82
9	**3i**	C_6H_5	C_6H_5(*R*)	H	**4i**	92
10	**3j**	C_6H_5	*i*-Bu(*S*)	H	**4j**	87
11	**3k**	*o*-HOC_6H_4	*i*-Bu(*S*)	H	**4k**	38
12	**3l**	C_6H_5	$-(CH_2)_4-$[c]		**4l**	59
13	**3m**	*o*-HOC_6H_4	$-(CH_2)_4-$[c]		**4m**	78
14	**3n**	*o*-$MeOC_6H_4$	$-(CH_2)_4-$[c]		**4n**	72

[a] Isolated yields. Each of all products was obtained as a single stereoisomer. See ref 6. [b] Prepared from racemic 1,2-diaminopropane. [c] Prepared from 1(*R*),2(*R*)-diaminocyclohexane.

Scheme I



3 **9** **10** **5** **11** **12** **10**

Results and Discussion

The reaction conditions of electroreduction were scrutinized by using *N,N'*-dibenzylideneethylenediamine (**3a**) as a typical substrate. The intramolecular coupling product, that is, *trans*-2,3-diphenylpiperazine (**4a**) was obtained in very high yield (95%) when the electroreduction was carried out with a lead cathode in dry DMF containing methanesulfonic acid (MsOH). The reaction gave similar results in dry acetonitrile. Using other cathode materials (Zn, Sn, and Pt) resulted in somewhat lower yields (80–90%).

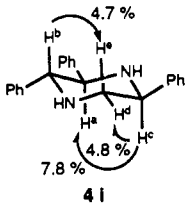
The presence of a strong protic acid such as MsOH was essential to promote the intramolecular coupling. When the reaction was carried out in the absence of MsOH, **4a** was not formed but *N,N'*-dibenzylethylenediamine was obtained as the main product (>60%). Trifluoroacetic acid was also effective while acetic acid brought about considerable decrease in the yield of **4a** (~30%).

The results obtained with other diimines are summarized in Table I. The electroreduction of diimines **3b–g** prepared from ethylenediamine and aromatic aldehydes gave *trans*-2,3-diarylpiperazines **4b–g** exclusively (runs 2–7). Tri- and tetrasubstituted piperazines **4h–n** were also obtained stereoselectively from diimines **3h–n** in reasonable yields (runs 8–14). Chiral piperazines were synthesized from chiral 1,2-diamines (runs 9–14). The protection of a hydroxy group on the aryl group was not always necessary (runs 5, 11, and 13).

Seven- and eight-membered cyclic compounds **6a,b**[8] were also obtained stereoselectively from **5a,b** by the same

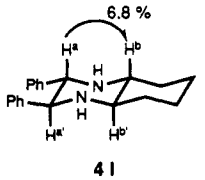
(5) Shono, T.; Kise, N.; Shirakawa, E. 56th Annual Meeting of the Chemical Society of Japan, April 1988, Abstr, p 1493.

(6) Stereochemistry of **4a** was determined through its N,N'-dimethylation and subsequent comparison of the ^1H NMR spectrum with the reported data.[7] Stereoconfigurations of **4i** and **4l** were assigned on the basis of reasonable coupling constants and NOE enhancements in their ^1H NMR (400 MHz).



4l

H^a δ 3.92 (d) J_{ab}=8.9 Hz
H^b δ 3.74 (d) J_{cd}=2.9 Hz
H^c δ 4.19 (dd) J_{de}=11.2 Hz
H^d δ 3.22 (dd) J_{ce}=10.4 Hz
H^e δ 2.99 (dd)



4l

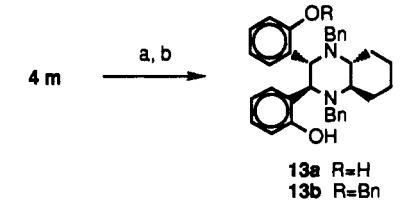
H^a δ 3.82 (s)
H^b δ 2.57–2.65 (m)

It seems reasonable that the other products **4b–4h**, **4j**, **4k**, **4m**, and **4n** have the same stereoconfigurations as **4a**, **4i**, and **4l**.

(7) Beugelmans, R.; Iguertsira, L. B.; Chastanet, J.; Negron, G.; Roussi, G. *Can. J. Chem.* **1985**, *63*, 725.

(8) The stereoconfigurations of **6a,b** were assigned to be trans by comparison with the samples prepared from *dl*-1,2-diamino-1,2-diphenylethane and 1,*n*-dibromoalkanes.

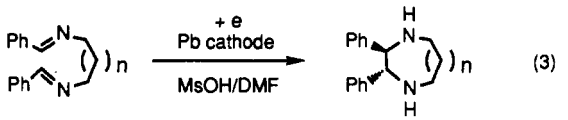
Scheme II



13a R=H
13b R=Bn

(a) (1) TMSCl (2 eq)/Et_3N/toluene, reflux, 1h, (2) BnBr (2 eq), reflux, 2h. (b) NaH (1.1 eq),/BnBr (1.2 eq),/THF, reflux, 2h.

method. The yields decreased with increasing the ring size (eq 3).

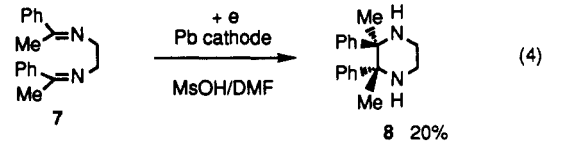


(3)

5a (n=1)
5b (n=2)

6a 79%
6b 30%

Diketoimines **7** also gave the corresponding intramolecularly coupled product **8**[9] stereoselectively, though the yield was relatively low (eq 4).



(4)

7

8 20%

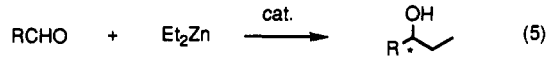
Reaction Mechanism. The electroreduction of **3a** in the absence of MsOH afforded the corresponding reduced amine (**12**) as described previously. In acidic media, however, diimines **3** were protonated to form diiminium salts **9** and the salts were electrochemically reduced. Two reaction pathways, that is, intramolecular radical coupling of a diradical intermediate **10** (path A) and nucleophilic addition of an anionic moiety of **11** to the intramolecular C=N bond (path B) may be depicted for the intramolecular coupling of **9** as shown in Scheme I. As the electrochemical reduction of imines has been known to exhibit two one-electron waves under acidic conditions,[10] the reduction of an iminium salt seems to proceed stepwise with forming a radical species as the first intermediate and an anion as the second intermediate. In addition, the observation of ESR spectra of the intermediate radicals has been reported in the electroreductive intermolecular coupling of iminium salts.[11] Hence, it is reasonable that one-electron reduction of the second iminium salt moiety of **9** will take place prior to reduction of the radical species formed by one-electron reduction of the first iminium salt moiety of **9**. Thus, the diradical species **10** is likely formed as the intermediate and the intramolecular coupling proceeds according to path A. The complete stereoselectivity may be explained by the fact that intermediate **10** is the most stable when it adopts a chair conformation in which all the substituents are located in equatorial positions.

Enantioselective Addition of Diethylzinc to Aldehydes in the Presence of a Chiral Piperazine. Chiral tri- and tetrasubstituted piperazines were easily synthesized from chiral 1,2-diamines by this electroreductive method (Table I, runs 9–14). These chiral piperazines are expected to be effective ligands of catalysts for the enantioselective synthesis of some chiral compounds. Chiral piperazines **13** prepared from **4m** (Scheme II), for example, were studied as chiral ligands in the reaction of aldehydes with diethylzinc (eq 5).[12] Bifunctional piperazine **13a** showed only moderate enantioselectivity, whereas monofunctional ligand **13b** derived by mono-*O*-benzylation of **13a** gave chiral secondary alcohols with high enantioselectivity (Table II).

Table II. Enantioselective Addition of Diethylzinc to Aldehydes

aldehyde	cat.	% yield[a]	% ee (config.)[b]	$[\alpha]^{25}_D$ (c, solvent)
PhCHO	**13a**	64	64[c] (*S*)	−28.8 (1.4, $CHCl_3$)
PhCHO	**13b**	85	>99[c] (*S*)	−46.8 (2.5, $CHCl_3$)
p-$MeOC_6H_4CHO$	**13b**	95	>99[c] (*S*)	−36.0 (5.1, benzene)
PhCH=CHCHO	**13b**	90	88[c] (*S*)	−7.2 (2.4, $CHCl_3$)
n-$C_6H_{13}CHO$	**13b**	91	81[d] (*S*)	+7.8 (5.0, $CHCl_3$)

[a] Isolated yields. [b] Determined by their optical rotations. Reported values are as follows: $[\alpha]_D$ −45.45 (*c* 5.15, $CHCl_3$) for (*S*)-1-phenylpropanol;[13] $[\alpha]_D$ −17.2 (*c* 5, benzene) for (*S*)-1-(4-methoxyphenyl)propanol in 51% ee;[14] $[\alpha]^{23}_D$ −6.6 (*c* 3.2, $CHCl_3$) for (*S*)-1-phenylpent-1-en-3-ol in 75% ee;[15] $[\alpha]^{24}_D$ +9.6 (*c* 8.3, $CHCl_3$) for (*S*)-3-nonanol.[16] [c] Determined by ^1H NMR of acetates of alcohols using $Eu(hfc)_3$. [d] Based on the optical rotation.



(5)

Experimental Section

IR spectra were recorded on a Hitachi 260-10 spectrometer. ^1H NMR and ^{13}C NMR spectra were measured on a Varian Gemini-200 or a JEOL JNM-GX400 spectrometer. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. Optical rotations were determined with a Perkin-Elmer 241 polarimeter. Melting points were uncorrected.

Starting Materials. Diimines **3**, **5**, and **7** were prepared from aromatic aldehydes or acetophenone and 1,*n*-diamines by refluxing their mixture in benzene.[17] (*R*)-1,2-Diamino-1-phenylethane and (*S*)-1,2-diamino-4-methylpentane were synthesized from (*R*)-phenylglycine and (*S*)-leucine, respectively, according to the reported method.[18] 1(*R*),2(*R*)-Diaminocyclohexane was obtained commercially.

General Procedure of Electroreduction. A solution of Et_4NOTs (4 g) in DMF (40 mL) was put into a divided cell (50-mL beaker) equipped with a lead cathode (5 × 10 cm^2), a carbon rod anode, and a ceramic diaphragm. To the catholyte were added a diimine **3** (10 mmol) and methanesulfonic acid (30 mmol). After electricity was passed with a constant current of 0.5 A (2.2 F/mol), the catholyte was poured into water (200 mL) and adjusted to pH 8 by addition of $NaHCO_3$. The product **4** was extracted with CH_2Cl_2 and isolated by recrystallization from hexane–AcOEt or column chromatography on Al_2O_3 (Activity III, hexane–AcOEt).

4a: mp 96–98 °C; IR (KBr) 3320, 3280, 2820, 1605, 1495, 860, 760, 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.95 (br s, 2 H, NH), 3.15 (s, 4 H), 3.72 (s, 2 H), 7.10 (s, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.98 (t), 68.18 (d), 127.30 (d), 127.88 (d), 128.13 (d), 141.53 (s). Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.67; H, 7.71; N, 11.62.

4b: mp 100–101 °C; IR (KBr) 3275, 2820, 1615, 1515, 820 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.77 (br s, 2 H, NH), 3.13 (s, 4 H), 3.63 (s, 2 H), 3.72 (s, 6 H), 6.62–6.73 (m, 4 H), 6.96–7.07 (m, 4 H);

(9) Although the stereostructure of **8** was not confirmed, it seems likely that it is trans.

(10) (a) Lund, H. *Acta Chem. Scand.* **1959**, *13*, 249. (b) Andrieux, C. P.; Saveant, J.-M. J. *Electronanal. Chem.* **1971**, *33*, 453.

(11) (a) Andrieux, C. P.; Saveant, J.-M. *J. Electroanal. Chem.* **1970**, *26*, 223. (b) *Ibid.* **1970**, *28*, 446.

(12) Recent studies on the enantioselective addition of diethylzinc to aldehydes in the presence of chiral amino alcohols: (a) Oguni, N.; Matsuda, Y.; Kaneko, T.; *J. Am. Chem. Soc.* **1988**, *110*, 7877. (b) Kitamura, M.; Okada, S.; Suga, S.; Noyori, R. *Ibid.* **1989**, *111*, 4028. (c) Soai, K.; Niwa, S. *Chem. Lett.* **1989**, 481.

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(14) Capillon, J.; Guette, J. *Tetrahedron* **1979**, *35*, 1817.

(15) Sato, T.; Gotoh, Y.; Wakabayashi, Y.; Fujisawa, T. *Tetrahedron Lett.* **1983**, *24*, 4123.

(16) Mukaiyama, T.; Hojo, K. *Chem. Lett.* **1976**, 893.

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^{13}C NMR (50 MHz, $CDCl_3$) δ 47.08 (t), 54.98 (q), 67.50 (d), 113.21 (d), 129.12 (d), 134.00 (s), 158.73 (s). Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.54; H, 7.47; N, 9.35.

4c: colorless paste; IR (neat) 3500–3000 (broad), 1740, 1590, 780, 740, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (br s, 2 H, NH), 3.13 (s, 4 H), 3.68 (s, 2 H), 4.88 (d, 2 H, J = 11.8 Hz), 4.92 (d, 2 H, J = 11.8 Hz), 6.63 (dd, 2 H, J = 1.2, 7.5 Hz), 6.70–6.80 (m, 4 H), 7.02 (dt, 2 H, J = 1.2, 7.5 Hz), 7.25–7.50 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.56 (t), 67.73 (d), 69.80 (t), 114.25 (d), 114.43 (d), 120.91 (d), 127.55 (s), 127.96 (d), 128.64 (d), 128.97 (d), 137.24 (s), 142.51 (s), 158.64 (s). Anal. Calcd for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.71; H, 6.65; N, 5.92.

4d: mp 122–125 °C; IR (KBr) 3325, 2800, 1595, 1490, 845, 825, 800 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.93 (br s, 2 H, NH), 3.11 (s, 4 H), 3.60 (s, 2 H), 6.96–7.03 (m, 4 H), 7.06–7.14 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.79 (t), 67.57 (d), 128.21 (d), 129.43 (d), 133.09 (s), 139.78 (s). Anal. Calcd for $C_{16}H_{16}N_2Cl_2$: C, 62.55; H, 5.25; N, 9.12; Cl, 23.08. Found: C, 62.45; H, 5.16; N, 8.99; Cl, 23.26.

4e: mp 177 °C; IR (KBr) 3300, 3500–2000 (broad), 1615, 1590, 1480, 765, 760, 745, 740 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.09–3.28 (m, 4 H), 4.06 (s, 2 H), 6.13 (dd, 2 H, J = 1.5, 7.6 Hz), 6.42 (dt, 2 H, J = 1.0, 7.6 Hz), 6.84 (dd, 2 H, J = 1.0, 7.6 Hz), 7.08 (dt, 2 H, J = 1.5, 7.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 45.02 (t), 63.13 (d), 116.64 (d), 118.64 (d), 123.33 (s), 129.12 (d), 130.20 (d), 157.15 (s). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.37. Found: C, 70.91; H, 6.69; N, 10.31.

4f: mp 102–105 °C; IR (KBr) 3600–3100 (broad), 1715, 1610, 765, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.11 (s, 2 H, NH), 3.20 (s, 4 H), 3.84 (s, 2 H), 3.86 (s, 6 H), 7.16 (d, 4 H, J = 8.2 Hz), 7.77 (d, 4 H, J = 8.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.14 (t), 51.92 (q), 67.35 (d), 128.18 (d), 129.46 (d), 129.62 (s), 145.21 (s), 167.01 (s). Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.69; H, 6.08; N, 7.87.

4g: mp 100–101 °C; IR (KBr) 3600, 3450, 3250, 2825, 1600, 1515, 795, 770 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.91 (br s, 2 H, NH), 3.22–3.40 (m, 4 H), 4.99 (s, 2 H), 7.08–8.20 (m, 14 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 47.63 (t), 60.26 (d), 122.50 (d), 125.07 (d), 125.20 (d), 125.56 (d), 127.78 (d), 128.57 (d), 131.59 (s), 133.65 (s), 137.44 (s). Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.00; H, 6.54; N, 8.26.

4h: mp 76–78 °C; IR (KBr) 3275, 2810, 1600, 1495, 805, 755, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.13 (d, 3 H, J = 6.4 Hz), 1.82 (br s, 2 H, NH), 2.71 (t, 1 H, J = 11.0 Hz), 3.12 (dd, 1 H, J = 2.7, 11.0 Hz), 3.11–3.23 (m, 1 H), 3.68 (d, 1 H, J = 9.0 Hz), 3.79 (d, 1 H, J = 9.0 Hz), 7.11 (s, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.90 (q), 51.91 (d), 54.21 (t), 67.64 (d), 68.38 (d), 127.12 (d), 127.75 (d), 128.02 (d), 141.28 (s), 141.44 (s). Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.79; H, 8.03; N, 11.14.

4i: mp 141–144 °C; $[\alpha]^{20}_D$ −121 (c 1.2, $CHCl_3$); IR (KBr) 3275, 2810, 1600, 1495, 800, 755, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (br s, 2 H, NH), 2.99 (dd, 1 H, J = 10.4, 11.2 Hz), 3.22 (dd, 1 H, J = 2.9, 11.2 Hz), 3.74 (d, 1 H, J = 8.9 Hz), 3.92 (d, 1 H, J = 8.9 Hz), 4.19 (dd, 1 H, J = 2.9, 10.4 Hz), 7.08–7.56 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.89 (t), 61.40 (d), 67.86 (d), 68.29 (d), 127.02 (d), 127.17 (d), 127.23 (d), 127.39 (d), 127.64 (d), 127.78 (d), 128.04 (d), 128.14 (d), 128.29 (d), 141.06 (s), 141.47 (s), 142.76 (s). Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.05; H, 7.05; N, 8.91. Found: C, 83.75; H, 7.15; N, 8.74.

4j: mp 73–76 °C; $[\alpha]^{20}_D$ +83 (c 1.0, $CHCl_3$); IR (KBr) 3275, 2810, 1600, 1495, 795, 755, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (d, 3 H, J = 6.5 Hz), 0.95 (d, 3 H, J = 6.5 Hz), 1.27–1.38 (m, 2 H), 1.57–1.76 (m, 1 H), 1.84 (br s, 2 H), 2.71 (t, 1 H, J = 10.7 Hz), 3.03–3.18 (m, 2 H), 3.68 (d, 1 H, J = 8.9 Hz), 3.78 (d, 1 H, J = 8.9 Hz), 7.11 (s, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.38 (q), 23.10 (q), 24.16 (d), 43.44 (t), 53.09 (t), 54.25 (d), 68.08 (d), 68.38 (d), 127.30 (d), 127.92 (d), 128.25 (d), 141.49 (s). Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.49; H, 8.87; N, 9.31.

4k: mp 182–183 °C; $[\alpha]^{20}_D$ +20 (c, 2.7, $CHCl_3$); IR (KBr) 3260, 3500–2000 (broad), 1610, 1585, 1470, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (d, 3 H, J = 6.4 Hz), 0.97 (d, 3 H, J = 6.4 Hz), 1.38 (t, 2 H, J = 6.4 Hz), 1.40–1.80 (m, 3 H), 2.73 (t, 1 H, J = 10.5 Hz), 3.05–3.25 (m, 2 H), 4.03 (d, 1 H, J = 9.8 Hz), 4.13 (d, 1 H, J = 9.8 Hz), 6.14 (d, 2 H, J = 7.5 Hz), 6.43 (t, 2 H, J = 7.5 Hz), 6.84 (d, 2 H, J = 7.5 Hz), 7.09 (t, 2 H, J = 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.13 (q), 23.00 (q), 23.98 (d), 42.95 (t), 50.91 (t), 52.81 (d), 62.96 (d), 63.25 (d), 116.65 (d), 118.70 (d), 123.18 (s), 123.38 (s), 129.13 (d), 130.22 (d), 157.09 (s). Anal. Calcd for $C_{20}H_{28}N_2O_2$: C, 73.58; H, 8.03; N, 8.58. Found: C, 73.25; H, 8.21; N, 8.58.

4l: mp 108–110 °C; $[\alpha]^{20}_D$ −70 (c 1.7, $CHCl_3$); IR (KBr) 3600–3100 (broad), 2800, 1600, 1495, 760, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30–1.50 (m, 4 H), 1.65–1.80 (m, 4 H), 1.70 (br s, 2 H, NH), 2.57–2.65 (m, 2 H), 3.82 (s, 2 H), 7.10 (s, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.71 (t), 31.61 (t), 61.45 (d), 68.41 (d), 127.19 (d), 127.88 (d), 128.17 (d), 141.56 (s). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.14; H, 8.27; N, 9.58. Found: C, 82.01; H, 8.19; N, 9.42.

4m: mp 215 °C; $[\alpha]^{20}_D$ −7.2 (c 1.7, $CHCl_3$); IR (KBr) 3300, 3600–2000 (broad), 1615, 1585, 1475, 765, 760, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20–1.90 (m, 8 H), 2.42 (br s, 2 H, NH), 2.65–2.75 (m, 2 H), 4.17 (s, 2 H), 6.13 (dd, 2 H, J = 1.4, 7.6 Hz), 6.43 (dt, 2 H, J = 1.0, 7.6 Hz), 6.84 (dd, 2 H, J = 1.4, 7.6 Hz), 7.08 (dt, 2 H, J = 1.0, 7.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.10 (t), 31.33 (t), 59.58 (d), 63.27 (d), 116.58 (d), 119.61 (d), 123.27 (s), 129.01 (d), 130.22 (d), 157.06 (s). Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.84; H, 7.56; N, 8.50.

4n: mp 110–111 °C; $[\alpha]^{20}_D$ +6.1 (c 3.3, $CHCl_3$); IR (KBr) 3700–3100 (broad), 1600, 1500, 755 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15–1.40 (m, 4 H), 1.60–1.80 (m, 6 H), 2.72 (br s, 2 H, NH), 3.69 (s, 6 H), 4.71 (br s, 2 H), 6.60–7.14 (m, 8 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.30 (t), 30.16 (t), 55.17 (d), 60.04 (d), 110.30 (d), 120.36 (d), 125.91 (s), 128.89 (d), 129.63 (d), 157.17 (s). Anal. Calcd for $C_{22}H_{28}N_2O_2$: C, 74.96; H, 8.01; N, 7.95. Found: C, 74.75; H, 7.89; N, 7.87.

6a: mp 90 °C; IR (KBr) 3380, 3350, 3050, 1600, 770, 750, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.80–2.00 (m, 2 H), 2.90–3.10 (m, 2 H), 3.20–3.40 (m, 2 H), 4.22 (s, 2 H), 6.90–7.10 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 36.60 (t), 48.32 (t), 68.34 (d), 126.95 (d), 128.05 (d), 142.67 (s). Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.76; H, 8.11; N, 10.64.

6b: mp 105 °C; IR (KBr) 3600–3100 (broad), 1610, 800, 760, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20–1.50 (m, 4 H), 2.70–2.90 (m, 2 H), 3.10–3.31 (m, 2 H), 4.09 (s, 2 H), 6.90–7.10 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 29.53 (t), 47.88 (t), 64.85 (d), 127.04 (d), 127.98 (d), 128.31 (d), 142.25 (s). Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.33; N, 10.52. Found: C, 81.18; H, 8.37; N, 10.33.

8: mp 130 °C; IR (KBr) 3325, 1605, 1495, 840, 780, 740, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.48 (s, 6 H), 2.96 (d, 2 H, J = 7.3 Hz), 3.50 (d, 2 H, J = 7.3 Hz), 7.22 (s, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.19 (q), 41.32 (t), 61.30 (s) 127,25 (d), 128.86 (d), 133.90 (d), 146.25 (s). Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.33; N, 10.52. Found: C, 81.17; H, 8.43; N, 10.44.

Synthesis of 13. Compound **13a** was obtained from **4m** by usual O-protection with TMSCl and subsequent N-alkylation with benzyl bromide in toluene as shown in Scheme II (73% yield). O-Benzylation of **13a** with 1.1 equiv of NaH and 1.2 equiv of benzyl bromide in THF gave **13b** (79% yield).

13a: mp 78–80 °C; $[\alpha]^{20}_D$ +26 (c 1.2, $CHCl_3$); IR (KBr) 3500–2000 (broad), 1585, 745, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10–1.48 (m, 4 H), 1.70–1.90 (m, 2 H), 2.40–2.65 (m, 4 H), 3.67 (d, 2 H, J = 16.0 Hz), 3.86 (s, 2 H), 4.15 (d, 2 H, J = 16.0 Hz), 5.98 (d, 2 H, J = 7.4 Hz), 6.41 (t, 2 H, J = 7.4 Hz), 6.77 (d, 2 H, J = 7.4 Hz), 6.90–7.35 (m, 12 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.72 (t), 30.92 (t), 53.11 (t), 62.98 (d), 67.41 (d), 116.67 (d), 119.13 (d), 124.32 (s), 127.89 (d), 128.76 (d), 129.20 (d), 130.12 (d), 131.82 (d), 135.50 (s), 157.08 (s). Anal. Calcd for $C_{34}H_{36}N_2O_2$: C, 80.92; H, 7.19; N, 5.55. Found: C, 80.93: H, 7.17: N, 5.33.

13b: mp 75 °C; $[\alpha]^{20}_D$ −50 (c 1.0, $CHCl_3$); IR (KBr) 3500–2000 (broad), 1595, 1500, 760, 740, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80–2.00 (m, 8 H), 2.50–2.70 (m, 2 H), 3.35 (d, 1 H, J = 16 Hz), 3.60–3.80 (m, 3 H), 4.22 (d, 1 H, J = 10.6 Hz), 4.24 (d, 1 H, J = 14.6 Hz), 4.54–4.64 (m, 2 H), 5.98 (d, 1 H, J = 7.5 Hz), 6.36 (t, 1 H, J = 7.5 Hz), 6.48 (d, 1 H, J = 7.5 Hz), 6.60 (d, 1 H, J = 7.5 Hz), 6.70–7.50 (m, 19 H), 7.60 (d, 1 H, J = 7.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.83 (t), 25.26 (t), 30.51 (t), 32.04 (t), 51.34 (t), 56.56 (t), 60.98 (d), 61.78 (d), 68.20 (d), 69.93 (t), 70.75 (d), 111.90 (d), 116.70 (d), 118.29 (d), 120.96 (d), 123.89 (s), 126.13 (d), 126.24 (d), 127.18 (d), 127.80 (d), 127.91 (d), 128.16 (d), 128.36 (d), 128.50 (d), 128.68 (d), 129.85 (d), 129.44 (d), 130.89 (d), 130.96

(d), 134.78 (s), 138.06 (s), 142.61 (s), 143.02 (s), 157.75 (s), 158.77 (s). Anal. Calcd for $C_{41}H_{42}N_2O_2$: C, 82.79; H, 7.12; N, 4.71. Found: C, 82.64: H, 7.06: N, 4.61.

General Procedure for Enantioselective Addition of Diethylzinc to Aldehydes. A mixture of diethylzinc (1 M hexane solution, 0.32 mL) and a chiral piperzine 13 (0.16 mmol) in toluene (5 mL) was refluxed for 30 min. Diethylzinc (1 M hexane solution, 4.8 mL) and an aldehyde (3.2 mmol) were added to the mixture at 0 °C. The mixture was stirred for 15–24 h at room temperature. After 1 N HCl (20 mL) was added, the mixture was extracted with CH_2Cl_2. The products, secondary alcohols, were isolated by PTLC (silica gel, hexane–AcOEt).

Bromination of Alkenes in Acetonitrile. A Rate and Product Study

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The reaction of simple alkenes and aryl alkenes with molecular bromine in damp MeCN occurred with solvent incorporation to give 2-bromo-1-(*N*-acetylamino)alkanes, 2-methyloxazolines, 2-acetoxyalkylamine hydrobromides, and 2-(*N*-acetylamino) alcohols. These products arose by the transformation of initially formed 2-bromo-1-(*N*-acetylamino)alkanes obtained by MeCN attack on bromonium or bromocarbonium ions to give nitrilium tribromide salts. These reacted with water to give 2-bromo-1-(*N*-acetylamino)alkanes. The kinetic profile of the reaction showed a very fast initial reaction of the alkene and Br_2 to yield the nitrilium tribromide, followed by a much slower reaction of Br_3^- with the alkene. The incorporation of MeCN was Markovnikov and stereospecifically anti. The degree to which incorporation of solvent occurred depended upon the alkene structure and the initial reagent concentrations. A rationalization for the observed chemoselectivity and its dependence on the reaction conditions is offered.

Introduction

Although the ionic bromination of alkenes[1] by molecular bromine in both aprotic[2] and protic[3] solvents of low polarity and in highly polar protic solvents[4] has been extensively studied, no systematic investigation of the reaction in polar aprotic solvents has been made. The halogenation of alkenes in such nucleophilic solvents can lead to the incorporation of solvent into the products.[5,6] The synthetic potential of such a reaction has been largely overlooked. For example, the reaction of chlorine and bromine with alkenes in MeCN has been reported[7] to give, as minor products, vicinal (*N*-acetylamino)haloalkanes. These arose from MeCN attack on halonium ion intermediates. It was later shown that the yield of such products could be increased if a stoichiometric amount of silver perchlorate was present in the reaction mixture. That additive prevented dibromide formation by scavenging the nucleophilic Br^- ions.[8] On the other hand, compounds that had incorporated MeCN were not observed during the bromination of *cis*- and *trans*-2-butene[3f] or *cis*- and *trans*-stilbene.[9]

To the best of our knowledge, no investigation of the rate of alkene bromination in MeCN has so far appeared in the literature. However, the bromination of *cis*- and *trans*-stilbene in valeronitrile has been reported.[10] This reaction exhibited a very peculiar kinetic course. A fast consumption of halogen was followed by a dramatic slowing of the reaction. No reasonable explanation was given for this behavior.

To obtain a more comprehensive picture of the reaction, we undertook a systematic product and kinetic study of alkene bromination in MeCN. The results showed that the incorporation of MeCN was general, regiospecific, and stereospecifically anti. The degree to which it occurred was markedly affected by both the structure of the alkene and by the reaction conditions.

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