Indirect Electroreductive Cyclisation of *N*-Allylic and *N*-Propargylbromo Amides and *o*-Bromoacryloylanilides using Nickel(II) Complexes as Electron-transfer Catalysts

Shigeko Ozaki,* Hidenori Matsushita and Hidenobu Ohmori
Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Yamadaoka, Suita, Osaka-fu 565, Japan

Nickel(II) complex-catalysed indirect electroreduction of *N*-allylic and *N*-propargyl-α-bromo amides and *o*-bromoacryloylanilides gave the corresponding 5-membered lactams. The product distribution was affected by the ability of the solvent to donate hydrogen atom. The electroreduction of *N*-allyl-*N*-(bromoacetyl)toluene-*p*-sulfonamide **1a** in DMF and acetonitrile yielded as main product the 4-methylpyrrolidinone **2a** (41%) and the 4-(bromomethyl)pyrrolidinone **3a** (33%), respectively. On addition of 2 mol equiv. of a hydrogen-atom donor (Ph_2PH) to the reaction of bromo amide **1a** in acetonitrile, compound **1a** provided compound **2a** (58%) as the sole cyclised product.

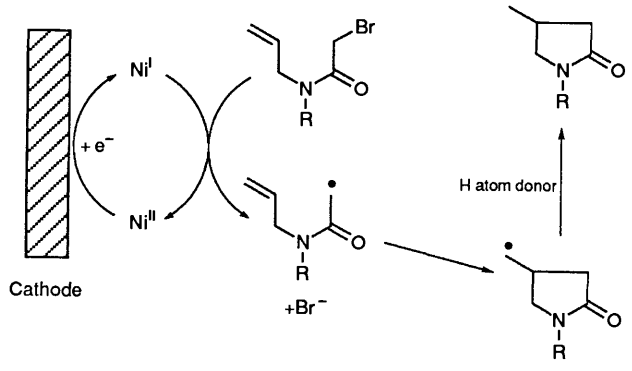
The construction of bicyclic lactams by radical cyclisation has attracted much interest, since lactams are attractive precursors of pyrrolidine-bearing bicyclic skeletons, which are components of various alkaloids or amino acid derivatives with potent physiological activities.[1] A number of useful studies on the construction of lactams by radical cyclisation of *N*-allylic-α-halogeno amides using tin hydride[2] or halogen atom-transfer methods[3] have been performed. It has been suggested that the radical cyclisation involving an amide group in the linking chain proceeds more slowly than that in the all-carbon counterpart[3d] because of restricted rotation around the amide [C(O)–N] bond, which retards the rate of isomerisation of amides into a conformer that can cyclise.[3d,4] Thus the success of this slow radical cyclisation, when the reactions are attempted by the tin hydride method, has been shown to depend strongly on the nature of substituents on both the α-position of the amide and the nitrogen which would affect the stability of both the initially generated radical and the cyclised one.[2b–d] However, in certain cases, the ability of the reaction temperature and substituents to change either the conformer population or the barrier to rotation[2c,d,5] seems to play a more important role in the successful cyclisation.

In our previous reports on nickel(II)-catalysed indirect electroreductive cyclisation of halogeno ethers[6] and 1,4-addition of alkyl radicals to activated olefins,[7] it has been shown that the electrochemical method is markedly different from the tin hydride method in that there is no active hydrogen-atom donor like tin hydride in the reaction system. This means that, in our method, hydrogenations of the initial radical and the cyclised one are much slower than those in the tin hydride method. Thus the present method will be useful especially for slow radical cyclisations that otherwise cannot compete with hydrogen abstraction. In the present work we performed formation of pyrrolidinones by indirect electroreduction of *N*-allylic and *N*-propargyl-α-bromo amides and *o*-bromoacryloylanilides, which probably proceeds according to Scheme 1, with two nickel(II) complexes **A** and **B** which exhibit Ni^{II}/Ni^{I} redox couples at −0.70 and −1.38 V *vs.* standard calomel electrode (SCE), respectively (Fig. 1), and explored the factors operating in cyclisations of these amides and anilides.

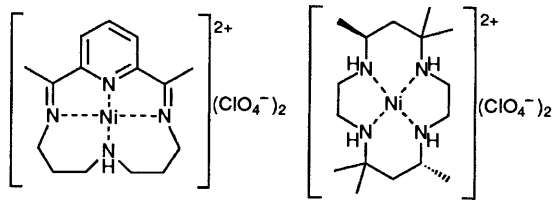
The reductive peak potentials of *N*-allylic-α-bromo amides and *o*-bromoacryloylanilides measured by cyclic voltammetry at a glassy carbon electrode are summarised in Table 1.

The α-bromo amides **1** are reduced electrochemically more easily than are simple alkyl bromides ($-E_{pc}$ 2.50–2.60 *vs.* SCE).

We checked by cyclic voltammetry, in a similar manner to that described previously,[7] whether electron transfer from the



Scheme 1



A **B**

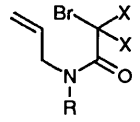
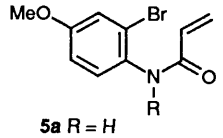
E_{pc}(V *vs.* SCE) −0.70 V −1.38V

Fig. 1

reductively generated nickel(I) complexes to the substrates occurs. The cathodic peaks of anilides **5a** and **5b** are possibly derived from reduction of the enone group. However, it could be assumed that electron transfer from electroreductively generated nickel(I) complexes occurs preferentially to the phenyl bromide group and not to the enone group of anilides **5**, since the electron transfer from complex **B** to an enone, cyclohex-2-enone, was not observed by voltammetric examinations.[7] Of nickel(II) complexes which showed cyclic voltammograms indicating that electron transfer to a substrate had occurred,† a nickel complex exhibiting the least negative redox potential was used as an electron-transfer catalyst in the electroreduction, *i.e.*, complexes **A** and **B** were used in reactions of the α-bromides and the *o*-bromoanilides, respectively. The reductive radical cyclisation of the α-bromo amides or *o*-bromoacryloylanilides was carried out potentiostatically at the

† Nickel(II) complexes examined, other than **A** and **B**, are nickel (tmc) $(ClO_4)_2$ and nickel (salen), which show the redox couples of (I)/(II) at −0.95 V and −1.68 V *vs.* SCE, respectively.

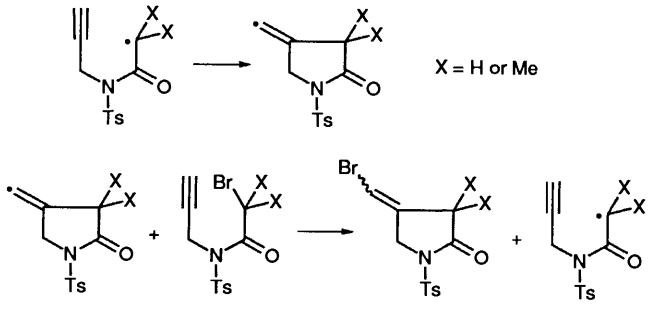
Table 1 Reduction peak potentials of α-bromo amides and *o*-bromoacryloylanilides[a]

Substrate	E_{pc}(V*vs.*SCE)
	
1a R = Ts, X = H	−1.63[b]
1b R = $CH_2CH{=}CH_2$, X = H	−1.94[b]
1c R = Bn, X = H	−1.90[b]
1d R = Ts, X = Me	−1.60[b]
	
5a R = H	−2.18[c]
5b R = Me	−2.32[c]

[a] Measured in DMF or acetonitrile containing Et_4NClO_4 (0.1 mol dm^{-3}) using 10 mmol dm^{-3} of a substrate at a glassy carbon electrode with a scan rate of 0.1 V s^{-1}. [b] Measured in acetonitrile. [c] Measured in DMF.

redox potential of a nickel(II) complex **A** or **B** by using substrate (1 or 0.5 mmol) and a nickel(II) complex (0.2 mol equiv.) in dimethylformamide (DMF) or acetonitrile (20 or 10 cm^3) containing a supporting electrolyte (Et_4ClO_4; 0.1 mol dm^{-3}) at a graphite cathode in an H-shaped divided cell under nitrogen. The results are listed in Table 2.

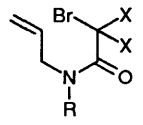
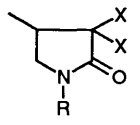
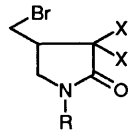
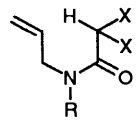
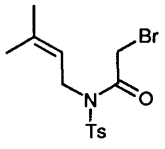
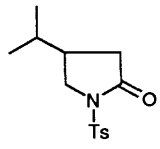
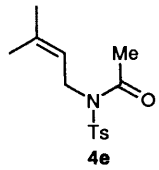
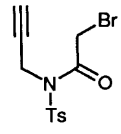
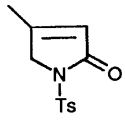
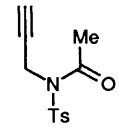
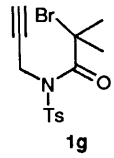
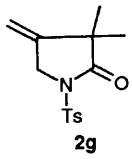
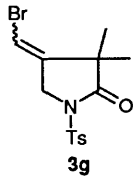
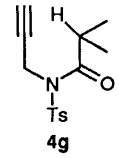
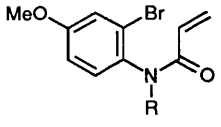
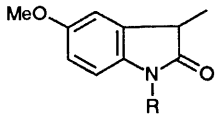
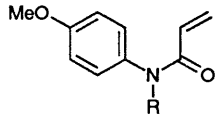
The reaction of amide **1a** in DMF afforded an expected cyclised product **2a**, along with 4-(bromomethyl)pyrrolidin-2-one **3a** and a simple reduction product **4a** in 41, 14, and 5% yield, respectively, while that in acetonitrile gave compound **3a** (33%) as the main product together with a small amount of compound **2a** (8%). These results seem to show that acetonitrile works less effectively as a hydrogen-atom donor than does DMF, and hence a cyclised radical formed in acetonitrile will tend to abstract a bromine atom from the starting amide. The 4-(bromomethyl)pyrrolidin-2-one **3a** was recovered unchanged when it was subjected to the electroreduction in the presence of 0.2 mol equiv. of nickel complex **A** at −0.70 V in DMF, which indicates that reduction of bromide **3a** to compound **2a** did not occur under the conditions used. The reaction of bromo amide **1a** in acetonitrile containing 2 mol equiv. of diphenylphosphine (PH_2PH), which has been used as an effective hydrogen-atom donor,[8] produced the pyrrolidinone **2a** as the sole cyclised product, in 58% yield, but also increased the amount of the reduction product **4a** (15%) (Table 2, run 3). We chose the reaction in acetonitrile with 2 mol equiv. of Ph_2PH as the preferable reaction conditions to obtain selectively non-brominated pyrrolidinones. Two other *N*-allylic bromoacetamides, **1b** and **1e**, gave the pyrrolidinones **2b** and **2e**, respectively, along with the reduction products in a similar yield as observed for compound **1a**. However, the reaction of the *N*-benzyl compound **1c** afforded the cyclised product **2c** in only 11% yield together with a large amount of the simple reduction product **4c** (63%). We speculated on the reason for these results following a comparison of the ^1H NMR spectra of compounds **1a** and **1c** with that of *N*-allyl-*N*-methyliodoacetamide which has been reported to exist as a mixture of two rotamers in CD_3Cl.[3d] In CD_3CN, allyl protons and bromomethyl protons of compound **1a** give resonances at δ 4.46 (2 H, dt, *J* 5.95 and 1.65 Hz, $CH_2CH{=}CH_2$) and 4.21 (2 H, s, CH_2Br), and in $CDCl_3$ at δ 4.46 (2 H, d, *J* 5.50, $CH_2CH{=}CH_2$) and 4.23 (2 H, s, CH_2Br), which indicates that compound **1a** exists as a sole rotamer in these solvents, or else that rotation around the amide bond [C(CO)–N] is very rapid. On the other hand, the ^1H NMR spectrum of compound **1c** suggests that it exists as a 2:1 mixture of two rotamers, *i.e.*, allyl and bromomethyl protons of major rotamer exhibit resonances at δ 3.92 (2 H, d, *J* 5.9) and 3.90 (2 H, s), respectively, and those of the minor rotamer at δ 4.02 (2 H, d, *J* 5.9) and 3.85 (2 H, s), respectively. This means that rotation around [C(CO)–N] is slow. The barriers to rotation in typical amides (16 ~ 22 kcal mol^{-1}),[4]* have been reported to be significantly higher than the activation energies for typical radical cyclisations (< 10 kcal mol^{-1}).[9] With this significant energy difference, the carbamoyl radicals generated from the typical amides seem likely to have still higher energy barriers to rotation than the activation energies for the radical cyclisations. Thus, when bromine is abstracted from compound **1c** by one-electron-transfers from the nickel(I) complex, the resulted carbamoyl radical is born in the almost 2:1 mixture of rotamers and a large part of the major radical might abstract a hydrogen atom before it isomerises into the (probably minor) rotamer that can cyclise. These results show that the radical cyclisation of *N*-allylic acetamides is strongly affected by the nature of substitution on the nitrogen, and tosylation is much better for protection of amino groups than is benzylation, though both groups are often used because of their ease of introduction and removal. In the case of amide substrates **1d** and **1g** which bear a tertiary bromide at the α-position of the amides, the brominated pyrrolidinones **3d** (8%) and **3g** (18%) were produced, respectively, together with the expected cyclised products **2d** (67%) and **2g** (33%) even in the presence of 2 mol equiv. of Ph_2PH. In cyclisations of hex-5-ynyl iodides conducted by the iodine-atom-transfer method, the rates of iodine transfer from tertiary iodides to vinyl radicals have been reported to be much larger than those from primary iodides.[10a,d,e] It has also been shown that sunlamp irradiation of hexenyl iodide in the presence of $(Bu_3Sn)_2$ gave (iodomethyl)cyclopentane and cyclohexyl iodide in total GLC yields > 70%.[10b] The driving force of the iodine-atom transfer from alkyl iodides to vinyl or alkyl radical has been attributed to the formation of a more stable radical from a less stable radical.[10c] Thus the driving force will be larger in reactions where stable tertiary alkyl radicals are generated at the expense of reactive vinyl or alkyl radicals. Though alkyl bromides are not so sufficiently reactive halogen-atom donors as are alkyl iodides towards vinyl or alkyl radicals to propagate the chain shown in Scheme 2, a bromine atom could transfer from the starting alkyl bromides to the more reactive vinyl or alkyl radicals. The result that more stable tertiary alkyl radicals are more conducive (Table 2, runs 6 and 9) than their less stable counterparts (runs 3 and 8) to cyclisation of carbamoyl radicals to give brominated products can be attributed to the difference in the driving force of bromine transfer.



Scheme 2

* 1 cal = 4.184 J.

Table 2 Electroreductive cyclisation of *N*-allylic and *N*-propargyl-α-bromo amides and *o*-bromoacryloylanilides using Ni^{II} complexes as electron-transfer catalysts[a]

Run	Substrate	Complex	Solvent	F/mol[b]	Product (yield %)[c]		
							
1	**1a** R = Ts, X = H	A	DMF	0.73	**2a** (41)	**3a** (14)	**4a** (5)
2	**1a**	A	MeCN	0.66	**2a** (8)	**3a** (33)	
3	**1a**	A	MeCN[d]	1.03	**2a** (58)		**4a** (15)
4	**1b** R = $CH_2CH{=}CH_2$, X = H	A	MeCN[d]	1.1	**2b** (50)		**4b** (25)
5	**1c** R = Bn, X = H	A	MeCN[d]	1.0	**2c** (11)		**4c** (63)
6	**1d** R = Ts, X = Me	A	MeCN[d]	1.0	**2d** (67)	**3d** (8)	**4d** (3)
7	 **1e**	A	MeCN[d]	1.1	 **2e** (49)		 **4e** (14)
8	 **1f**	A	MeCN[d]	0.9	 **2f** (7)		 **4f** (37)
9	 **1g**	A	MeCN[d]	0.9	 **2g** (33)	 **3g** (18)[e]	 **4g** (10)
							
10	**5a** R = H	B	DMF	2.7	**6b** (23)		**7a** (26)
11	**5b** R = Me	B	DMF	2.8			

[a] For conditions, see text. [b] Electricity for the conversion of the substrate. [c] Isolated yield based on initial substrate. [d] Electrolysis in the presence of 2 mol equiv. of Ph_2PH. [e] Mixture of diastereoisomers (5:1).

In the cyclisation of the acryloylanilides, an *N*-methylated anilide **5b** provided an indoline **6b** (23%), while a secondary anilide **5a** gave only a simple reduction product **7a** (26%) in accord with the suggestion of Jones and McCarthy[5] that alkylation of the nitrogen of the *o*-bromoacryloylanilides is essential for the successful radical cyclisation. The reason why the *N*-alkylation is necessary for the cyclisation can be explained in part by the reports of Pedersen and Chupp[11] on the rotational isomers of α-halogeno acetanilides, demonstrating the the predominant conformer of *N*-methylated anilides exists in a form with the NMe group *cis* to the carbonyl oxygen, *i.e.* in the form that can cyclise, while that of secondary α-halogeno anilides is fixed in the rotamer with the NH group *trans* to the carbonyl oxygen. We have shown that the present method can afford the cyclised products in good yield at room temperature starting from *N*-allylic and *N*-propargyl-α-bromo amides which

tend to yield only the simple reduction product in attempted cyclisation by the tin hydride method unless the structures of the starting amides are highly suitable for cyclisation.

Experimental

Instrumentation.—NMR spectra were taken on a JEOL EX-270 or Varian VXR-200 instrument. *J* Values are given in Hz. IR spectra were taken on a JASCO A-202 instrument. Cyclic voltammetry was performed with a three-electrode system employing a linear scanning unit (Huso Electrochemical System HECS 321B) equipped with a potentiostat (Hokuto Denko PS-55B). Controlled-potential electrolysis was carried out with a potentiostat (Hokuto Denko HA 301 or HA 105S), and the quantity of electricity consumed was recorded with a coulometer (Hokuto Denko HF-201).

Materials.—N-*Allyl*-N-(*bromoacetyl*)*toluene*-p-*sulfonamide* **1a**. A solution of bromoacetyl bromide (8.07 g, 40 mmol) in benzene (10 cm^3) was added dropwise to a mixture of NaH (4.0 g, 100 mmol; 60% in oil) and *N*-allyltoluene-*p*-sulfonamide (5.3 g, 25 mmol) in benzene (30 cm^3) at 0 °C. After being stirred for 3 h at 60 °C the reaction mixture was poured into cold water (50 cm^3) and extracted with diethyl ether. The extract was washed successively with 1 mol dm^{-3} aq. NaOH and brine. Purification of the crude product by silica gel column chromatography yielded compound **1a** (1.9 g, 23%), m.p. 89–90 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1700 (amide), 1645 (CH=CH_2) and 1360 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 2.46 (3 H, s, Me), 4.23 (2 H, s, CH_2Br), 4.46 (2 H, d, *J* 5.5, CH_2N), 5.19–5.34 (2 H, m, CH=CH_2), 5.75–5.97 (1 H, m, C*H*=CH_2), 7.36 (2 H, d, *J* 9, ArH) and 7.84 (2 H, d, *J* 9, ArH).

N,N-*Diallylbromoacetamide* **1b**. A solution of bromoacetyl bromide (8.04 g, 40 mmol) in carbon tetrachloride (5 cm^3) was added to a mixture of diallylamine (3.88 g, 40 mmol) and triethylamine (6.06 g, 60 mmol) in CCl_4 (30 cm^3) at 0 °C. After being stirred for 15 h at room temperature the mixture was treated with 1 mol dm^{-3} aq. K_2CO_3 (50 cm^3) and extracted with methylene dichloride. Purification of the crude product by silica gel column chromatography yielded compound **1b** as an oil (0.96 g, 11%), ν_{max}(neat)/cm^{-1} 1645 (amide); δ_H(200 MHz; $CDCl_3$) 3.84 (2 H, s, CH_2Br), 3.99 (4 H, m, 2 × CH_2N), 5.10–5.32 (4 H, m, 2 × CH=CH_2) and 5.65–5.95 (2 H, m, 2 × C*H*=CH_2).

N-*Allyl*-N-*benzylbromoacetamide* **1c**. A solution of bromoacetyl bromide in CCl_4 (3 cm^3) was added dropwise to a mixture of *N*-allyl-*N*-benzylamine and triethylamine in CCl_4 (20 cm^3) at 0 °C. After being stirred for 15 h the reaction mixture was diluted with 0.5 mol dm^{-3} aq. K_2CO_3 and extracted with CH_2Cl_2. Purification of the crude product by silica gel column chromatography yielded compound **1c** as a pale yellow oil (1.54 g, 57%), ν_{max}(neat)/cm^{-1} 1660 (amide); δ_H(270 MHz; $CDCl_3$) (major rotamer) 3.90 (2 H, s, CH_2Br), 3.92 (2 H, d, *J* 5.9, CH_2N), 4.61 (2 H, s, CH_2Ph), 5.09–5.31 (2 H, m, CH=CH_2), 5.68–5.90 (1 H, m, C*H*=CH_2) and 7.15–7.42 (5 H, m, Ph); (minor rotamer) 3.85 (2 H, s, CH_2Br), 4.02 (2 H, d, *J* 5.9, CH_2N), 4.61 (2 H, s, CH_2Ph), 5.09–5.31 (2 H, m, CH=CH_2), 5.68–5.90 (1 H, m, C*H*=CH_2) and 7.15–7.42 (5 H, m, Ph).

N-*Allyl*-N-(2-*bromo*-2-*methylpropionyl*)*toluene*-p-*sulfonamide* **1d**. A solution of *N*-allyltoluene-*p*-sulfonamide (2.11 g, 10 mmol) in benzene (15 cm^3) and a solution of bromoacetyl bromide (4.60 g, 20 mmol) in benzene (10 cm^3) were successively added dropwise to a mixture of NaH (0.60 g, 20 mmol; 80% in oil) in benzene (10 cm^3) and the mixture was heated at 50 °C for 7 h. The cooled reaction mixture was added to 1 mol dm^{-3} aq. NaOH (50 cm^3), extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Successive purification of the crude product by silica gel column chromatography and recrystallisation from hexane–AcOEt gave compound **1d** as a solid (2.78 g, 77%), m.p. 83–84 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1680 (amide), 1650 (CH=CH) and 1360 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.89 (6 H, s, 2 × Me), 2.44 (3 H, s, MeAr), 4.96 (2 H, d, *J* 5, CH_2N), 5.34 (1 H, d, *J* 10, CH_aH_b=CH), 5.42 (1 H, d, *J* 17, CH_aH_b=CH), 5.88–6.08 (1 H, m, C*H*=CH_2), 7.30 (2 H, d, *J* 8, ArH) and 7.87 (2 H, d, *J* 8, ArH).

N-*Bromoacetyl*-N-(3-*methylbut*-2-*enyl*)*toluene*-p-*sulfonamide* **1e**. Compound **1e** was prepared by a similar method to that used for compound **1a** as a solid (2.09 g, 60%), m.p. 47–48 °C; ν_{max}(neat)/cm^{-1} 1700 (amide), 1655 (CH=CH) and 1360 and 1150 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.72 (6 H, s, 2 × Me), 2.45 (3 H, s, *Me*Ar), 4.25 (2 H, s, CH_2Br), 4.44 (2 H, d, *J* 7, CH_2N), 5.14 (1 H, m, CH=C), 7.35 (2 H, d, *J* 8, ArH) and 7.80 (2 H, d, *J* 8, ArH).

N-*Bromoacetyl*-N-*propargyltoluene*-p-*sulfonamide* **1f**. Solutions of *N*-propargyltoluene-*p*-sulfonamide (1.0 g, 4.78 mmol) in dry benzene (5 cm^3) and bromoacetyl bromide (2.0 g, 10 mmol) in benzene (5 cm^3) were successively added dropwise to a mixture of NaH (150 mg, 5 mmol; 80% in oil) in benzene (5 cm^3) and the mixture was heated at 50 °C for 10 h. The cooled reaction mixture was added to cold 1 mol dm^{-3} aq. NaOH, extracted with diethyl ether, washed with brine, and dried over $MgSO_4$. Successive purification of the crude product by column chromatography and recrystallisation from hexane–AcOEt gave compound **1f** as a solid (490 mg, 31%), m.p. 109–111 °C; $\nu_{max}(CHCl_3)$ 3300 (≡CH), 1710 (amide) and 1370 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 2.29 (1 H, t, *J* 2.6, C≡CH), 2.46 (3 H, s, *Me*Ar), 4.25 (2 H, s, CH_2Br), 4.68 (2 H, d, *J* 2.6, CH_2N), 7.37 (2 H, *J* 8, ArH) and 7.91 (2 H, d, *J* 8, ArH).

N-(2-*Bromo*-2-*methylpropionyl*)-N-*propargyltoluene*-p-*sulfonamide* **1g**. *N*-Propargyltoluene-*p*-sulfonamide (0.80 g, 3.82 mmol) and 2-bromo-2-methylpropionyl bromide (2.29 g, 10 mmol) were successively added dropwise to NaH (120 mg, 4 mmol; 80% in oil) and the mixture was heated at 50 °C for 10 h. A similar work-up of the reaction mixture and purification to that used in the preparation of compound **1f** gave compound **1g** as a solid, m.p. 92–93 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3300 (≡CH), 1690 (amide) and 1360 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.95 (6 H, s, 2 × Me), 2.45 (3 H + 1 H, *Me*Ar and C≡CH), 5.14 (2 H, d, *J* 2, CH_2N), 7.32 (2 H, d, *J* 8, ArH) and 7.99 (2 H, d, *J* 8, ArH).

o-*Bromo*-p-*methoxyacryloylanilide* **5a**. Dicyclohexylcarbodiimide (DCC) (10 mmol) was added to a solution of acrylic acid (720 mg, 10 mmol) in CH_2Cl_2 (20 cm^3) at 0 °C and the reaction mixture was stirred for 15 min, then *o*-bromo-*p*-methoxyaniline was added and the mixture was stirred for 12 h. The solid mass was removed by filtration. Purification by silica gel column chromatography yielded compound **5a**, m.p. 120–121 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (NH) and 1680 (amide); δ_H(200 MHz; $CDCl_3$) 3.78 (3 H, s, OMe), 5.78 (1 H, dd, *J* 9.6 and 1.6, CH=CH_aH_b), 6.28 (1 H, dd, *J* 16.8 and 9.6, C*H*=CH_2), 6.44 (1 H, dd, *J* 16.8 and 1.6, CH=CH_aH_b), 6.88 (1 H, dd, *J* 9.1 and 2.7, ArH), 7.09 (1 H, d, *J* 2.7, ArH), 7.58 (1 H, br, NH) and 8.24 (1 H, d, *J* 9.1, ArH).

o-*Bromo*-p-*methoxy*-N-*methylacryloylanilide* **5b**. A solution of *o*-bromo-*p*-methoxyacryloylanilide **5a** (380 mg, 1.48 mmol) in tetrahydrofuran (THF) (10 cm^3) was added dropwise to a mixture of NaH (49.5 mg, 1.65 mmol; 80% in oil) in THF (5 cm^3) at 0 °C under nitrogen and after being stirred for 10 min was treated slowly with methyl iodide (750 mg, 5.3 mmol); then the reaction mixture was stirred for 12 h. After replacement of the solvent by Et_2O (100 cm^3), the solution was washed with brine. Purification of the crude product by column chromatography yielded compound **5b** as an oil which solidified on storage, m.p. 65–66 °C; ν_{max}(neat)/cm^{-1} 1660 (amide); δ_H(200 MHz; $CDCl_3$) 3.24 (3 H, s, MeN), 3.83 (3 H, s, MeO), 5.51 (1 H, dd, *J* 10.3 and 2.0, CH=CH_aH_b), 5.91 (1 H, dd, *J* 16.6 and 10.3,

C*H*=CH_2), 6.37 (1 H, dd, *J* 16.6 and 2.0, CH=CH_aH_b) 6.89 (1 H, dd, *J* 8.7 and 2.8, ArH), 7.17 (1 H, d, *J* 8.7, ArH) and 7.20 (1 H, d, *J* 2.8, ArH).

N-Allyltoluene-*p*-sulfonamide was prepared by a literature method[12] in 71% yield as a solid, m.p. 61–62 °C; ν_{max}($CHCl_3$)/cm^{-1} 1645 (CH=CH) and 1330 and 1160 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 2.43 (3 H, s, Me), 3.60 (2 H, m, CH_2N), 4.73 (1 H, br, NH), 5.08 (1 H, d, *J* 12, CH=CH_aH_b), 5.15 (1 H, d, *J* 18, CH=CH_aH_b), 5.6–5.85 (1 H, m, C*H*=CH_2), 7.31 (2 H, d, *J* 8, ArH) and 7.76 (2 H, d, *J* 8, ArH).

N-Allyl-*N*-benzylamine was prepared by a literature method[12] in 29% yield as an oil; ν_{max}(neat)/cm^{-1} 3320 (NH) and 1645 (CH=CH); δ_H(200 MHz; $CDCl_3$) 3.28 (2 H, d, *J* 6, CH_2CH=CH_2), 3.79 (2 H, s, CH_2Ph), 5.12 (1 H, d, *J* 10, CH=CH_aH_b), 5.19 (1 H, d, *J* 20, CH=CH_aH_b), 5.83–6.03 (1 H, m, C*H*=CH_2) and 7.20–7.40 (5 H, m, Ph).

N-(3-Methylbut-2-enyl)toluene-*p*-sulfonamide was prepared by heating a mixture of 3-methylbut-2-enyl bromide (12.1 g, 80 mmol), toluene-*p*-sulfonamide (24 g, 140 mmol) and K_2CO_3 (16.5 g, 120 mmol) in MeCN (150 cm^3). Purification by silica gel column chromatography yielded the sulfonamide (37%) as a solid, m.p. 48–49 °C; ν_{max}(neat)/cm^{-1} 3260 (NH), 1675 (CH=C) 1330 and 1160 (sulfonamide); δ_H(270 MHz; $CDCl_3$) 1.53 (3 H, s, Me_aMe_bC=), 1.62 (3 H, s, Me_aMe_bC=), 2.49 (3 H, s, *Me*Ar), 3.53 (2 H, m, CH_2N), 4.53 (1 H, br, NH), 5.05 (1 H, m, CH=C), 7.30 (2 H, d, *J* 8, ArH) and 7.76 (2 H, d, *J* 8, ArH).

N-Propargyltoluene-*p*-sulfonamide was prepared by reaction of toluene-*p*-sulfonamine (25.6 g, 0.15 mol), propargyl bromide (9.52 g, 0.08 mol) and K_2CO_3 (21 g, 0.15 mol) in MeCN (100 cm^3) at 60 °C for 20 h. The solid mass was removed by filtration. Purification by silica gel column chromatography gave a solid, m.p. 67–68 °C; ν_{max}($CHCl_3$) 3380 (NH), 3300 (≡CH) and 1340 and 1160 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 2.10 (1 H, t, *J* 2.6, CH≡C), 2.43 (3 H, s, Me), 3.83 (2 H, m, CH_2N), 4.6–4.8 (1 H, NH), 7.32 (2 H, d, *J* 8, ArH) and 7.76 (2 H, d, *J* 8, ArH).

o-Bromo-*p*-methoxyaniline was prepared by a literature method[13] (27%) as a red oil; δ_H(200 MHz; $CDCl_3$) 3.5 (2 H, br, NH_2), 3.73 (3 H, s, MeO), 6.72 (2 H, m, ArH) and 7.00 (1 H, m, ArH).

2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II) perchlorate, complex **A**, and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) perchlorate, complex **B**, were prepared by the literature methods.[14,15] Complex **A**: 66%, reddish brown needles, m.p. 272–273 °C (decomp.); complex **B**: 81%, orange amorphous crystals, m.p. > 280 °C (decomp.).

Tetraethylammonium perchlorate was prepared by addition of aq. tetraethylammonium bromide to perchloric acid (70%) and was recrystallised successively from hot water and ethanol. Other reagents were purchased and used as received.

Controlled-potential Electrolysis and Product Analysis.—An acetamide, propionamide (1 mmol) or anilide (0.5 mmol), and a nickel complex **A** or **B** (0.2 mol equiv. based on the substrate) were dissolved in DMF (20 or 10 cm^3) or MeCN (20 cm^3) containing Et_4NClO_4 (0.1 mol dm^{-3}) in an H-shaped divided cell. NH_4ClO_4 (2 mol equiv.) was added in the electrolysis of the anilides. The electrolyte was degassed by bubbling nitrogen through it for 20 min, after which it was electrolysed potentiostatically using a graphite plate as a cathode at the redox potential of nickel complex **A** or **B**, *i.e.* at −0.70 V or −1.30 V *vs.* SCE at room temperature under nitrogen until complete consumption of the acetamide, propionamide or anilide. The products, extracted with diethyl ether from the electrolyte which had been diluted with water, were separated by column chromatography (silica gel). Spectral data and analytical results of the products are as follows. 4-Methyl-1-tosylpyrrolidin-2-one **2a**, a solid; m.p. 84–85 °C (Found: C, 56.65; H, 5.9; N, 5.5. Calc. for $C_{12}H_{15}NO_3$: C, 56.90; H, 5.97; N, 5.53%); ν_{max}($CHCl_3$)/cm^{-1} 1740 (lactam) and 1365 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.09 (3 H, d, *J* 6, *Me*CH), 2.06 (1 H, dd, *J* 16.0 and 6.8, CH_aH_bCO), 2.44 (3 H, s, *Me*Ar), 2.35–2.65 (2 H, m, MeC*H* and CH_aH_bCO), 3.41 (1 H, dd, *J* 9.8 and 6.4, CH_aH_bN), 4.03 (1 H, dd, *J* 9.8 and 7.2, CH_aH_bN), 7.34 (2 H, d, *J* 8, ArH) and 7.91 (2 H, d, *J* 8, ArH).

1-Allyl-4-methylpyrrolidin-2-one **2b**, an oil; ν_{max}(neat)/cm^{-1} 1690 (lactam); δ_H(270 MHz; $CDCl_3$) 1.12 (3 H, d, *J* 6.6, Me), 2.04 (1 H, dd, *J* 16.2 and 9.6, CH_aH_bCO), 2.42 (1 H, m, C*H*Me), 2.58 (1 H, dd, *J* 16.2 and 7.6, CH_aH_bCO), 2.93 (1 H, dd, *J* 9.6 and 5.6, CH_aH_bN), 3.46 (1 H, dd, *J* 9.6 and 7.6, CH_aH_bN), 3.87 (2 H, d, *J* 6.3, CH_2CH=CN_2), 5.11–5.23 (2 H, m, CH=CH_2) and 5.62–5.80 (1 H, m, C*H*=CH_2).

1-Benzyl-4-methylpyrrolidin-2-one **2c**, an oil; ν_{max}(neat)/cm^{-1} 1685 (lactam); δ_H(200 MHz; $CDCl_3$) 1.07 (3 H, d, *J* 6.6, Me), 2.08 (1 H, dd, *J* 16.1 and 6.4, CH_aH_bCO), 2.41 (1 H, m, C*H*Me), 2.61 (1 H, dd, *J* 16.1 and 8.4, CH_aH_bCO), 2.82 (1 H, dd, *J* 9.5 and 5.9, CH_aH_bN), 3.36 (1 H, dd, *J* 9.5 and 7.7, CH_aH_bN), 4.43 (2 H, s, CH_2Ph) and 7.20–7.40 (5 H, m, Ph). 3,3,4-Trimethyl-1-tosylpyrrolidin-2-one **2d**, a solid; m.p. 136–138 °C (Found: C, 59.6; H, 6.7; N, 5.0. Calc. for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98%); ν_{max}($CHCl_3$)/cm^{-1} 1735 (lactam) and 1365 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 0.80 (3 H, s, Me), 0.97 (3 H, d, *J* 7, *Me*CH), 1.06 (3 H, s, Me), 2.11 (1 H, m, C*H*Me), 2.43 (3 H, s, *Me*Ar), 3.26 (1 H, dd, *J* 9.6 and 9.6, CH_aH_bN), 3.96 (1 H, dd, *J* 9.6 and 7.6, CH_aH_bN), 7.32 (2 H, d, *J* 8, ArH) and 7.90 (2 H, *J* 8, ArH).

4-Isopropyl-1-tosylpyrrolidin-2-one **2e**, a solid; m.p. 105–106 °C (Found: C, 59.4; H, 6.7; N, 5.0. Calc. for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98%); ν_{max}($CHCl_3$)/cm^{-1} 1735 (lactam) and 1360 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 0.86–0.95 (6 H, m, Me_2CH), 1.53 (1 H, m, C*H*Me_2), 2.00–2.23 (2 H, CH_aH_bCO and C*H*CH_2CO), 2.40–2.58 (4 H, m, CH_aH_bCO and *Me*Ar), 3.44 (1 H, t, *J* 9.2, CH_aH_bN), 4.05 (1 H, dd, *J* 7.6 and 9.9, CH_aH_bN), 7.34 (2 H, d, *J* 8, ArH) and 7.92 (2 H, d, *J* 8, ArH).

4-Methyl-1-tosylpyrrol-2(5*H*)-one **2f**, a solid; m.p. 159–160 °C (Found: C, 57.1; H, 5.3; N, 5.5. Calc. for $C_{12}H_{13}NO_3S$: C, 57.35; H, 5.21; N, 5.57%); ν_{max}($CHCl_3$)/cm^{-1} 1725 (lactam) and 1640 (C=CH); δ_H(200 MHz; $CDCl_3$) 2.08 (3 H, s, Me), 2.43 (3 H, s, *Me*Ar), 4.33 (2 H, s, CH_2N), 5.74 (1 H, s, CH=C), 7.32 (2 H, d, *J* 8, ArH) and 7.94 (2 H, d, *J* 8, ArH); δ_C(67.8 MHz; $CDCl_3$) 121.94 (C=*C*HCO) and 159.82 (*C*=CHCO).

3,3-Dimethyl-4-methylene-1-tosylpyrrolidin-2-one **2g**, a solid; m.p. 104–106 °C (Found: C, 60.2; H, 6.0; N, 4.9. Calc. for $C_{14}H_{17}NO_3$: C, 60.19; H, 6.14; N, 5.01%); ν_{max}($CHCl_3$)/cm^{-1} 1740 (lactam), 1670 (CH_2=C) and 1365 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.16 (6 H, s, 2 × Me), 2.44 (3 H, s, *Me*Ar), 4.45 (2 H, m, CH_2N), 5.06 (1 H, m, CH_aH_b=C), 5.10 (1 H, m, CH_aH_b=C), 7.33 (2 H, d, *J* 8, ArH) and 7.93 (2 H, d, *J* 8, ArH).

4-Bromomethyl-1-tosylpyrrolidin-2-one **3a**, a solid; m.p. 92–94 °C (Found: C, 43.4; H, 4.2; N, 4.1. Calc. for $C_{12}H_{14}BrNO_3S$: C, 43.4; H, 4.25; N, 4.2%); ν_{max}($CHCl_3$)/cm^{-1} 1740 (lactam); δ_H(270 MHz; $CDCl_3$) 2.34 (1 H, dd, *J* 17.5 and 7.3, CH_aH_bCO), 2.44 (3 H, s, Me), 2.64 (1 H, dd, *J* 17.5 and 8.6, CH_aH_bCO), 2.80 (1 H, m, C*H*CH_2Br), 3.38 (2 H, m, CH_2Br), 3.69 (1 H, dd, *J* 10.3 and 6.3, CH_aH_bN), 4.09 (1 H, dd, *J* 10.3 and 7.9, CH_aH_bN), 7.35 (2 H, d, *J* 8, ArH) and 7.92 (2 H, d, *J* 8, ArH).

4-Bromomethyl-3,3-dimethyl-1-tosylpyrrolidin-2-one **3d**, a solid; m.p. 133–135 °C; ν_{max}($CHCl_3$)/cm^{-1} 1740 (lactam) and 1365 and 1170 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 0.90 (3 H, s, Me), 1.16 (3 H, s, Me), 2.44 (3 H + 1 H, s and m, *Me*Ph and C*H*CH_2Br), 3.21 (1 H, dd, *J* 10 and 3, CH_aH_bN), 3.45 (2 H, m, CH_2Br), 4.15 (1 H, dd, *J* 10.3 and 7.4, CH_aH_bN), 7.34 (2 H, d, *J* 8, ArH) and 7.92 (2 H, d, *J* 8, ArH).

4-Bromomethylene-3,3-dimethyl-1-tosylpyrrolidin-2-one **3g** (major isomer), a solid; m.p. 126–128 °C; ν_{max}($CHCl_3$)/cm^{-1}

1740 (lactam) and 1370 and 1175 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.21 (6 H, s, 2 × Me), 2.45 (3 H, s, *Me*Ar), 4.43 (2 H, d, *J* 2.7, CH_2N), 6.16 (1 H, m, CH=C), 7.35 (2 H, d, *J* 8, ArH) and 7.95 (2 H, d, *J* 8, ArH); (minor isomer), a solid, m.p. 153–155 °C; *m/z* 360 and 358 (M^+); ν_{max}($CHCl_3$)/cm^{-1} 1740 (lactam), 1650 (C=CH) and 1370 and 1175 (sulfonamide); δ_H(200 MHz; $CDCl_3$) 1.40 (6 H, s, 2 × Me), 2.45 (3 H, s, *Me*Ar), 4.40 (2 H, d, *J* 2.0, CH_2N), 6.19 (1 H, m, CH=C), 7.34 (2 H, d, *J* 8, ArH) and 7.92 (2 H, d, *J* 8, ArH).

N-Acetyl-*N*-allyltoluene-*p*-sulfonamide **4a**, δ_H(200 MHz, $CDCl_3$) 2.29 (3 H, s, MeCO), 2.44 (3 H, s, *Me*Ar), 4.47 (2 H, d, *J* 5.5, CH_2N), 5.24 (1 H, d, *J* 10, CH_aH_b=CH), 5.28 (1 H, d, *J* 17, CH_aH_b=CH), 5.8–6.0 (1 H, m, CH_2=C*H*), 7.34 (2 H, d, *J* 8, ArH) and 7.81 (2 H, d, *J* 8, ArH).

N,*N*-Diallylacetamide **4b**, an oil; ν_{max}(neat)/cm^{-1} 1650 (amide); δ_H(200 MHz; $CDCl_3$) 2.10 (3 H, s, Me), 3.87 [2 H, d, *J* 4.4, $C(H_a)_2N$], 3.99 [2 H, d, *J* 5.9, $C(H_b)_2N$], 5.08–5.25 (4 H, m, 2 × CH_2=CH) and 5.68–5.88 (2 H, m, 2 × C*H*=CH_2).

N-Allyl-*N*-benzylacetamide **4c**, an oil; ν_{max}(neat)/cm^{-1} 1650 (amide); δ_H(200 MHz; $CDCl_3$) assigned to major rotamer: 2.16 (3 H, s, MeCO), 3.82 (2 H, d, *J* 4.8, CH_2N), 4.59 (2 H, s, CH_2Ph), 5.03–5.29 (2 H, m, CH_2=CH), 5.68–5.92 (1 H, m, C*H*=CH_2) and 7.19–7.40 (5 H, m, Ph); assigned to minor rotamer: 2.16 (3 H, s, MeCO), 4.02 (2 H, d, *J* 6, CH_2N), 4.51 (2 H, s, CH_2Ph), 5.03–5.29 (2 H, m, CH_2=CH), 5.68–5.92 (1 H, m, C*H*=CH_2) and 7.19–7.40 (5 H, m, Ph).

N-Allyl-*N*-isobutyryltoluene-*p*-sulfonamide **4d**, an oil; δ_H (200 MHz; $CDCl_3$) 1.02 (6 H, d, *J* 7, 2 × Me), 2.44 (3 H, s, *Me*Ar), 3.09 (1 H, m, CHCO), 4.50 (2 H, d, *J* 6, CH_2N), 5.19–5.33 (2 H, m, CH_2=CH), 5.80–6.00 (1 H, m, C*H*=CH_2), 7.32 (2 H, d, *J* 8, ArH) and 7.80 (2 H, d, *J* 8, ArH).

N-Acetyl-*N*-(3-methylbut-2-enyl)toluene-*p*-sulfonamide **4e**, δ_H(200 MHz; $CDCl_3$) 1.73 (6 H, s, Me_2C=CH), 2.29 (3 H, s, MeCO), 2.44 (3 H, s, *Me*Ar), 4.55 (2 H, d, *J* 7, CH_2N), 5.19 (1 H, m, C*H*=CMe_2), 7.32 (2 H, d, *J* 8, ArH) and 7.78 (2 H, d, *J* 8, ArH).

N-Acetyl-*N*-propargyltoluene-*p*-sulfonamide **4f**, a solid; δ_H (200 MHz; $CDCl_3$) 2.29 (1 H, C≡CH), 2.33 (3 H, s, MeCO), 2.46 (3 H, s, *Me*Ar), 4.67 (2 H, d, *J* 2.4, CH_2N), 7.35 (2 H, d, *J* 8, ArH) and 7.91 (2 H, d, *J* 8, ArH).

N-Isobutyryl-*N*-propargyltoluene-*p*-sulfonamide **4g**, an oil; δ_H(200 MHz; $CDCl_3$) 1.02 (6 H, d, *J* 6, 2 × Me), 2.32 (1 H, t, *J* 2, CH≡C), 2.45 (3 H, s, *Me*Ar), 3.15 (1 H, m, CHCO), 4.69 (2 H, d, *J* 2, CH_2N), 7.35 (2 H, d, *J* 8, ArH) and 7.91 (2 H, d, *J* 8, ArH).

5-Methoxy-1,3-dimethylindol-2-(3*H*)-one **6b**, a solid; m.p. 78–80 °C; ν_{max}($CHCl_3$)/cm^{-1} 1700 (lactam); δ_H(270 MHz; $CDCl_3$) 1.47 (3 H, d, *J* 7.6, *Me*CH), 3.18 (3 H, s, MeN), 3.41 (1 H, q, *J* 7.6, C*H*Me), 3.80 (3 H, s, OMe) and 6.70–6.89 (3 H, m, ArH).

p-Methoxyacryloylanilide **7a**, a solid; m.p. 95–96 °C; ν_{max} ($CHCl_3$)/cm^{-1} 3300 (NH) and 1680 (CH=CH); δ_H(200 MHz; $CDCl_3$) 3.84 (3 H, s, MeO), 5.70 (1 H, dd, *J* 9.6 and 2.0, CH_aH_b=CH), 6.24 (1 H, dd, *J* 16.8 and 9.7, C*H*=CH_2), 6.40 (1 H, dd, *J* 16.7 and 2.0, CH_aH_b=CH), 6.84 (2 H, d, *J* 8.8, ArH), 7.48 (2 H, d, *J* 8.8, ArH) and 7.76 (1 H, br, NH).

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Paper 3/01893H
Received 20*th April* 1993
Accepted 8*th June* 1993