for sensory applications, and c) the incorporation of Mn into a cyclophane framework, which provides a more economical building block than Re for nonluminescent applications.

Experimental Section

Bimetallic [{(CO)$_4$M}$_2$BiBzIm] edges[15] (BzIm = benzimidazolate) were formed by stirring [M(CO)$_5$X] (M, X = Mn, Br or Re, Cl) with K$_2$[BiBzIm][16, 17] at ambient temperature in CH$_2$Cl$_2$. At the reaction endpoint (monitored by FTIR), the solvent was partially removed and the desired [{(CO)$_4$M}$_2$BiBzIm] product precipitated as a yellow (**1a**) or white (**1b**) powder by addition of Et$_2$O (45 % yield).[18] Rectangular cycles were obtained by reacting equimolar amounts of the bimetallic edge with 4,4′-bpy in refluxing THF for two days. Hexanes were added to the flask after cooling to room temperature. Further cooling provided orange-yellow crystals (**2a**) or a bright yellow powder (**2b**) at ~70 % yield.[19, 20] Thin films of **2a** and **2b** were cast evaporatively from filtered THF/CHCl$_3$ (1/1) solutions.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139036. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The UV/Vis absorption spectra of **1b** and **2b** are found in the Supporting Information.

Received: February 2, 2000 [Z 14635]

---

[1] M. Fujita, K. Ogura, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471, and references therein.

[2] P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502, and references therein.

[3] W.-H. Leung, J. Y. K. Cheng, T. S. M. Hun, C.-M. Che, W.-T. Wong, K.-K. Cheung, *Organometallics* **1996**, *15*, 1497.

[4] H. A. Cruse, N. E. Leadbeater, *Inorg. Chem.* **1999**, *38*, 4149.

[5] S.-S. Sun, A. J. Lees, *Inorg. Chem.* **1999**, *38*, 4181.

[6] S. M. Woessner, J. B. Helms, J. F. Houlis, B. P. Sullivan, *Inorg. Chem.* **1999**, *38*, 4380.

[7] R. V. Slone, K. D. Benkstein, S. Bélanger, J. T. Hupp, I. A. Guzei, A. L. Rheingold, *Coord. Chem. Rev.* **1998**, *171*, 221, and references therein.

[8] R. V. Slone, D. I. Yoon, R. M. Calhoun, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 11813.

[9] For the experimental setup, see: M. H. Keefe, R. V. Slone, J. T. Hupp, K. F. Czaplewski, R. Q. Snurr, *Langmuir* **2000**, in press.

[10] a) K. D. Benkstein, J. T. Hupp, C. L. Stern, *Inorg. Chem.* **1998**, *37*, 5404; b) K. D. Benkstein, J. T. Hupp, C. L. Stern, *J. Am. Chem. Soc.* **1998**, *120*, 12982.

[11] See also: S. M. Woessner, J. B. Helms, Y. Shen, B. P. Sullivan, *Inorg. Chem.* **1998**, *37*, 5406.

[12] Charged, fluxionally rectangular *organic* cyclophanes are known, see: B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1988**, *100*, 1605; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1547.

[13] Crystal data for **2a**: crystal dimensions 0.5 × 0.4 × 0.2 mm; monoclinic; space group $P2_1/n$ (No. 14); $a = 16.501(1)$, $b = 20.195(1)$, $c = 13.587(1)$ Å, $\beta = 102.864(1)°$, $V = 4414.1(5)$ Å^3; $Z = 2$; $\rho_{calc} = 1.316$ g cm^{-3}; $2\theta_{max} = 69.5°$; Mo$_{K\alpha}$ radiation, $\lambda = 0.7107$ Å; scan mode ω; $T = 153$ K; 40889 reflections, of which 10900 are unique, and of which 6063 were included in the refinement; data corrected for Lorentz polarization effects; solution by direct methods (SIR92 A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **1993**, *26*, 343) and refinement on $|F^2|$ by full-matrix least-squares procedures (TeXsan for Windows v1.03, Molecular Structure Corporation, Texas, USA); 535 parameters; isotropic refinement of disordered solvent atoms, the remaining nonhydrogen atoms were refined anisotropically; H atoms were included, except in disordered solvent molecules, but not refined; final values $R|F| = 0.059$, $R_w|F| = 0.090$.

[14] G. Z. Sauerbrey, *Physica* **1959**, *155*, 206.

[15] R. Uson, J. Gimeno, *J. Organomet. Chem.* **1981**, *220*, 173.

[16] M. C. Rezende, C. A. Marques, E. L. Dall'Oglio, C. Zucco, *Liebigs Ann.* **1997**, 925.

[17] M. P. Gamasa, E. Garcia, J. Gimeno, C. J. Ballesteros, *Organomet. Chem.* **1986**, *307*, 39.

[18] **1b**: ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.67$ (q, $J = 3$ Hz, 4H), 7.42 (q, $J = 3$ Hz, 4H). FTIR (CH$_2$Cl$_2$): $\tilde{\nu} = 2113$ (w; CO), 2019, 1989, 1949 cm^{-1}. LR-MS: **1b**·2CO: calcd: $m/z = 772.7$; found: 773.0. Elemental analysis: calcd: C 31.88, H 0.92, N 6.76; found: C 31.66, H 0.97, N 6.50.

[19] **2a**: ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 8.02$ (d, $J = 7$ Hz, 8H), 7.92 (q, $J = 3$ Hz, 8H), 7.42 (q, $J = 2$ Hz, 8H), 7.20 (d, $J = 7$ Hz, 8H). FTIR (THF): $\tilde{\nu} = 2031$ (sh; CO), 2029, 1940, 1919 cm^{-1}. FAB-MS: calcd: $m/z = 1332.7$; found: 1332.3. Elemental analysis: calcd: C 54.07, H 2.42, N 12.61; found: C 53.39, H 3.00, N 12.67. Cyclic voltammetry: reversible reductions (versus ferrocene): −1.76 V (bpy$^{-/0}$/bpy^0), −1.97 V (bpy$^-$/bpy$^{-/0}$), −2.42 V (multielectron wave).

[20] **2b**: ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 8.13$ (d, $J = 6$ Hz, 8H), 7.83 (q, $J = 3$ Hz, 8H), 7.43 (q, $J = 3$ Hz, 8H), 6.77 (d, $J = 6$ Hz, 8H). FTIR (THF): $\tilde{\nu} = 2026$ (sh; CO), 2023, 1921, 1908 cm^{-1}. FAB-MS: calcd: $m/z = 1857.8$; found: 1858.1. Elemental analysis (**2b**·1THF): calcd: C 39.83, H 2.09, N 8.71; found: C 39.50, H 2.44, N 8.12. Cyclic voltametry: reversible reductions (versus ferrocene): −1.47 V (bpy$^{-/0}$/bpy^0), −1.70 V (bpy$^-$/bpy$^{-/0}$), −2.28 V, −2.43 V.

Enantioselective Synthesis of 4-Unsubstituted 3-Alkoxy- and 3-Aminoazetidin-2-ones from Formaldehyde *N*,*N*-Dialkylhydrazones**

Rosario Fernández, Ana Ferrete, José M. Lassaletta,*
José M. Llera,* and Angeles Monge

The presence of the azetidin-2-one ring in several widely used families of antibiotics, which include the penicillins and carbapenems, has stimulated considerable activity directed at the stereocontrolled synthesis of β-lactams.[1] One of the most popular methods is the [2+2] cycloaddition reaction of ketenes to imines (the Staudinger reaction).[2] The particular

---

[*] Dr. J. M. Lassaletta
Instituto de Investigaciones Químicas (CSIC-USe)
c/ Americo Vespuccio s/n, Isla de la Cartuja
41092 Sevilla (Spain)
Fax: (+34) 95-446-0565
E-mail: jmlassa@cica.es

Dr. J. M. Llera
Dpto. de Química Orgánica y Farmacéutica
Universidad de Sevilla
41081 Sevilla (Spain)
Fax: (+34) 954 233 765
E-mail: llera@fafar.us.es

Dr. R. Fernández, A. Ferrete
Dpto. de Química Orgánica
Universidad de Sevilla, Seville (Spain)

Dr. A. Monge
Instituto de Ciencia de Materiales de Madrid, CSIC
Madrid (Spain)

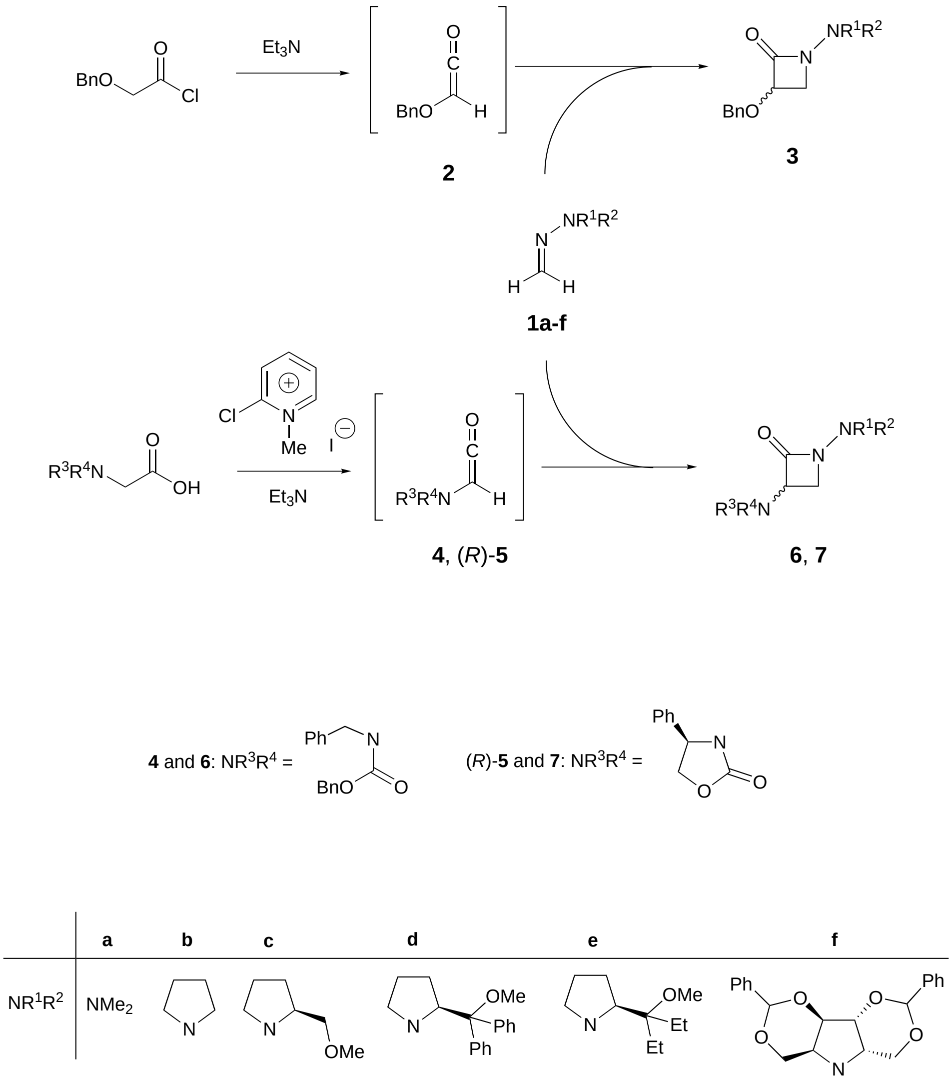
[**] We thank the Dirección General de Investigación Científica y Técnica for financial support (Grant no. PB 97/0747). We also thank the Ministerio de Educación y Ciencia for a doctoral fellowship to A.F.

case of 4-unsubstituted 2-azetidinones merits special attention for its presence in nocardicins and monobactams, as well as in other bioactive compounds such as tabtoxin[3] and the pachystermines.[4] In this case, however, the cycloaddition approach requires the use of formaldehyde-derived imines (methanimines), which tend to tri- and oligomerize under the reaction conditions.[5] Hence, indirect, longer routes to these compounds are required.[6]

During our recent work on the chemistry of formaldehyde *N*,*N*-dialkylhydrazones we have regularly observed their high stability as monomers, even at high temperatures and in the presence of bases and some Lewis acids.[7] This fact and the availability of several hydrazones containing tunable chiral auxiliaries prompted us to explore the usefulness of these compounds, viewed now as electron-rich, *N*-aminosubstituted imines, for the asymmetric synthesis of β-lactams by cycloaddition to ketenes.[8]

First experiments were performed using achiral hydrazones **1a** and **1b**, and in situ generated benzyloxyketene (**2**; Scheme 1) as model compounds. Reactions carried out in toluene led to the formation of the desired cycloadducts **3a** and **3b** in 84 and 67% yield, respectively (Table 1, entries 1 and 2), with the first reaction (from **1a**) being a much cleaner reaction. This difference suggests that the higher nucleophilicity of **1b**[7d,e] results in competing side reactions at its azomethine carbon. In addition, a strong influence of the solvent was recognized: use of chloroform, CH_2Cl_2, THF, or Et_2O resulted in the formation of complex mixtures, where 1-benzyloxy-3-(pyrrolidin-1-ylimino)-propan-2-one or its dimethyl analogue (1,2 adducts to the ketene) were found as major products.

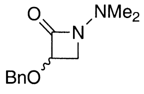
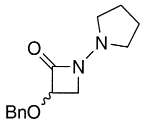
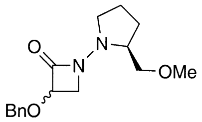
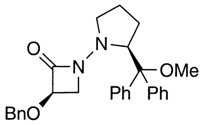
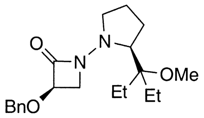
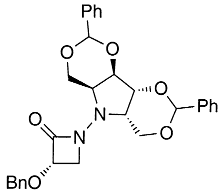
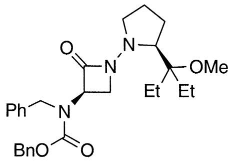
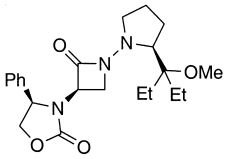
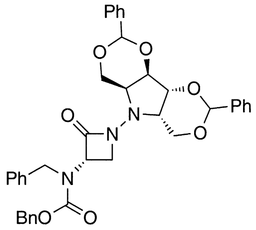
Formaldehyde SAMP hydrazone **1c**[7b] reacted with ketene **2** in a similar way (entry 3), but the low inductions observed prompted us to investigate the behavior of easily available hydrazones **1d**[7e] and **1e**,[7e] which have bigger (quaternary) residues at position 2. The higher steric hindrance in these reagents resulted not only in the expected increase of selectivity in the cycloaddition (d.r. values of 81:19 and 84:16 for **3d** and **3e**, respectively) but, also, in the inhibition of the above-mentioned side reactions, as demonstrated by the almost quantitative yields obtained (entries 4 and 5). The use of hydrazone **1e** had additional advantages: in this case, both diastereoisomers (*R*,*S*)- and (*S*,*S*)-**3e** could be easily separated by flash chromatography, thus affording a satisfactory 80% yield of the major diastereomer (*R*,*S*)-**3e** in a single step. Finally, the behavior of the C_2-symmetric reagent **1f** was also investigated. The interest for this particular reagent arises from several remarkable singularities. First, a better stereoselectivity could be expected due to the benefits frequently observed for C_2-symmetric auxiliaries.[9] Second, the presence of two neighboring groups at both sides (C-2 and C-5) of the C–N double bond and the rigidity conferred by the condensed 1,3 dioxane rings should hinder the planar conformation associated with the competing nucleophilic reactivity of the azomethine carbon.[10] Third, the parent hydrazine can be prepared in bulk quantities from inexpensive D-mannitol in a few steps.[11] A single isomer **3f** was detected in this case and isolated in 89% yield (entry 6). As expected considering the relative stereochemistry of **1e** and **1f**, **3f** had *S* configuration at C-3, the opposite configuration to the major isomer of **3e**.



Scheme 1. [2+2] Cycloaddition reaction of formaldehyde *N*,*N*-dialkylhydrazones **1** to alkoxy and aminoketenes **2**, **4**, and (*R*)-**5**. Bn = Benzyl.

The cycloaddition of hydrazones **1e** and **1f** to α-amino-

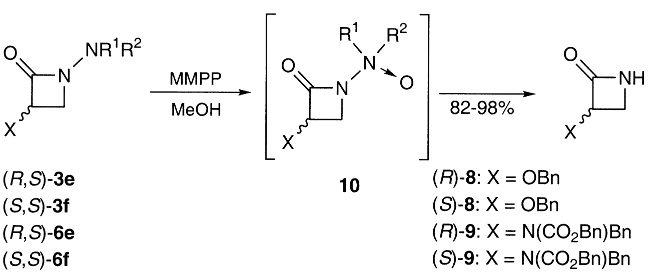
Table 1. [2+2] Cycloaddition of formaldehyde *N,N*-dialkylhydrazones with ketenes. Synthesis of 1-amino-3-alkoxyazetidin-2-ones and 1,3-diaminoazetidin-2-ones.

Entry	Ketene	Hydrazone	Cycloadduct	*T*[a]	*t*[b]	d.r.[c]	Configuration at C-3[d]	Yield [%][e]
1	**2**	**1a**	 **3a**	RT	48	–	–	84
2	**2**	**1b**	 **3b**	RT	26	–	–	57
				50	2.5	–	–	67
3	**2**	**1c**	 **3c**	RT	50	50:50[f]	*R*/*S*	80
				80	2.5	50:50[f]	*R*/*S*	89
4	**2**	**1d**	 **3d**	RT	6 d	85:15[f]	*R*	85
				80	3.5	81:19[f]		96
5	**2**	**1e**	 **3e**	RT	24	85:15	*R*	89 (75)
				80	1.5	84:16		96 (80)
6	**2**	**1f**	 **3f**	80	7	>99:1	*S*	89
7	**4**	**1e**	 **6e**	80	23	82:18	*R*	93 (76)
8	(*R*)-**5**	**1e**	 **7e**	80	9	>99:1	*R*	94
9	**4**	**1f**	 **6f**	60	8	>99:1	*S*	81

[a] Units = °C. RT = Room temperature. [b] Units = hours unless otherwise stated. [c] Determined by ^{13}C and ^{1}H NMR spectroscopy. [d] Configuration of the major isomer. [e] Yield after isolation by flash chromatography. Values in parentheses correspond to the pure (*de* = 98 %) major isomer. [f] Inseparable mixture of diastereomers.

ketenes **4** and (*R*)-**5** was also investigated. In this case, the best results were obtained by using suitable α-amino acid derivatives and 2-chloro-*N*-methyl pyridinium iodide[12] for the generation of the ketene. Under these conditions, adduct **6e** was obtained in 93% yield as a 82:18 mixture of diastereomers (entry 7), which could also be separated by means of simple flash chromatography to yield adducts (*R*,*S*)- and (*S*,*S*)-**6e** in optically pure form. As expected, a "matched" double induction experiment using (*R*)-**5**[13] afforded the corresponding adduct **7e** as a single diastereoisomer (entry 8). In addition, compound **6f**, which has the opposite *S* configuration at C-3, was also obtained in good yield as a single diastereoisomer from the reaction of **1f** with **4** (entry 9).

The key N–N bond cleavage needed for the release of the chiral auxiliaries of adducts **3** and **6** was unsuccessful by catalytic hydrogenolysis (Raney Ni, Pd/C, and $Pd(OH)_2/C$) or by Li/NH_3 under several conditions, while use of SmI_2[14] required the presence of HMPA as cosolvent and gave moderate yields of product (**8**: 64–65% from **3e,f**; **9**: 42% from **6e**). Inspired in the Meisenheimer rearrangement[15] of tertiary amine oxides, we decided to investigate the oxidative N–N bond cleavage promoted by magnesium monoperoxyphthalate (MMPP). This unprecedented deamination method efficiently afforded the desired products (82–89% yield; Scheme 2, Table 2), which are presumably formed by the homolytic cleavage of the N–N bond of intermediate hydrazide N(sp^3) oxides **10**.[16]



Scheme 2. MMPP-promoted oxidative N–N bond cleavage of compounds **3** and **6** to form compounds **8** and **9**.

Table 2. Oxidative N–N bond cleavage of adducts **3** and **6** promoted by MMPP. Synthesis of compounds **8** and **9**.

Adduct	X[a]	Product	Time [h]	Yield [%]	$[\alpha]_D^{22}$[b]
(*R*,*S*)-**3e**	OBn	(*R*)-**8**	1	89	+54.9
3f	OBn	(*S*)-**8**	6	82	−55.9
(*R*,*S*)-**6e**	$N(CO_2Bn)Bn$	(*R*)-**9**	1	83	+8.0
6f	$N(CO_2Bn)Bn$	(*S*)-**9**	6	83	−8.8

[a] See Scheme 2. [b] ($c = 1$, CH_2Cl_2).

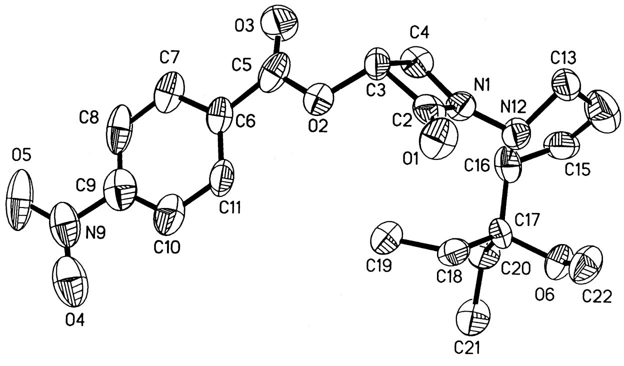
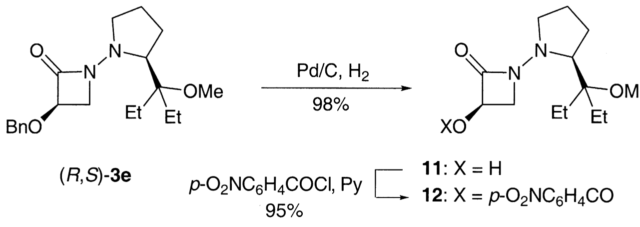
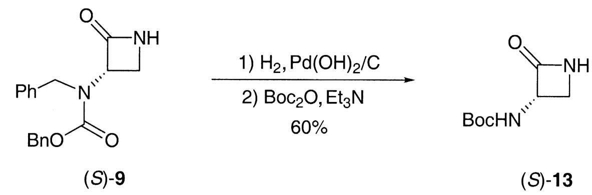


Figure 1. Crystal structure of (*R*,*S*)-**12**.



Scheme 3. Synthesis of (*R*,*S*)-**12**. Py = pyridine.



Scheme 4. Synthesis of (*S*)-**13**. Boc = *tert*-butoxycarbonyl.

The absolute configuration of (*R*,*S*)-**3e** was determined by X-ray diffraction analysis[17] (Figure 1) of the *p*-nitrobenzoyl derivative **12**, obtained from the former after hydrogenolysis (→**11**) and esterification (Scheme 3). The opposite 3*S* configuration of **3f** was determined by comparison of the optical rotation of (*R*)-**8** ($[\alpha]_D^{20} = +54.9$ ($c = 1$, CH_2Cl_2)) and (*S*)-**8** ($[\alpha]_D^{20} = -55.9$ ($c = 0.9$, CH_2Cl_2)), obtained from (*R*,*S*)-**3e** and **3f**, respectively. Finally, (*S*)-**9** ($[\alpha]_D^{20} = -8.8$ ($c = 1$, CH_2Cl_2)) was transformed into (*S*)-**13** (Scheme 4) and its optical rotation was compared to the literature data;[18] (*R*)-**9** had the opposite sign ($[\alpha]_D^{20} = +8.0$ ($c = 1$, CH_2Cl_2)).

In summary, a new entry to enantiopure 4-unsubstituted 3-alkoxy and 3-amino β-lactams has been developed which consists of two efficient steps: (1) the [2+2] cycloaddition reaction of chiral formaldehyde *N*,*N*-dialkylhydrazones to alkoxy or aminoketenes, and (2) the MMPP-promoted oxidative N–N bond cleavage of the resulting hydrazides. Both *R*- and *S*-configured products can be easily synthesized starting from L-proline or D-mannitol derived hydrazones **1e** and **1f**, respectively. It is important to emphasize that the chiral auxiliaries act as N-protecting groups at the same time, thereby reducing the number of steps required to reach the final targets.

Experimental Section

Adducts **3**: Benzyloxyacetyl chloride (2 mmol) in toluene (5 mL) was added to a solution of hydrazone **1** (1 mmol) and Et_3N (4 mmol) in dry toluene (10 mL). The mixture was stirred at 80 °C until completion. Adducts **6** and **7**: 2-Chloro-*N*-methyl pyridinium iodide (0.82–1.65 mmol) and Et_3N (1.5–4.5 mmol) were added to a solution of the glycine derivative (0.75 or 1.5 mmol) in toluene (4.5 mL). **1** (0.3 mmol) was then added and the mixture was stirred at 80 °C until completion.

Compounds **8** and **9**: MMPP·$6H_2O$ (0.9–1.8 mmol) was added to a solution of **3** or **6** (0.3 mmol) in MeOH (0.5–0.75 mL) and the mixture was stirred at RT until completion.

Received: February 3, 2000 [Z 14642]

[1] Reviews: a) R. J. Ternansky, J. M. Morin, Jr. in *The Organic Chemistry of β-Lactams* (Ed.: G. I. Georg), VCH, New York, **1993**, p. 257; b) L. Ghosez, J. Marchand-Brynaert in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: B. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 85.

[2] H. Staudinger, *Liebigs Ann. Chem.* **1907**, *356*, 51.

[3] T. Kikuchi, T. Nishinaga, S. Uyeo, O. Yamashiro, K. Minami, *Tetrahedron Lett.* **1968**, 909.

[4] a) G. M. Salitura, C. A. Townsend, *J. Am. Chem. Soc.* **1990**, *112*, 760; b) C. Cativiela, M. Díaz de Villegas, J. A. Gálvez, *Tetrahedron: Asymmetry* **1994**, *5*, 1465.

[5] As a remarkable exception, *N*-methylene[bis(trimethylsilyl)methyl]-amine has recently been described as a stable, monomeric compound suitable for cycloaddition reactions with ketenes: C. Palomo, J. M. Aizpurua, M. Legido, R. Lagarza, *Chem. Commun.* **1997**, 233.

[6] a) B. Alcaide, A. Rodríguez-Vicente, M. A. Sierra, *Tetrahedron Lett.* **1998**, *39*, 163; b) B. Alcaide, L. Casarrubios, G. Domínguez, M. A. Sierra, *J. Org. Chem.* **1994**, *59*, 7943; c) B. Alcaide, M. Aly, M. A. Sierra, *J. Org. Chem.* **1996**, *61*, 8819; d) S. D. Sharma, U. Mehra, J. P. S. Khurana, S. B. Pandhi, *Synthesis* **1987**, 990; e) A. Arrieta, B. Lecea, F. P. Cossío, C. Palomo, *J. Org. Chem.* **1987**, *53*, 3784.

[7] Selected references: a) J. M. Lassaletta, R. Fernández, *Tetrahedron Lett.* **1992**, *33*, 3691; b) D. Enders, R. Syrig, G. Raabe, R. Fernández, C. Gasch, J. M. Lassaletta, J. M. Llera, *Synthesis* **1996**, 48; c) J. M. Lassaletta, R. Fernández, E. Martín-Zamora, E. Díez, *J. Am. Chem. Soc.* **1996**, *118*, 7002; d) J. M. Lassaletta, R. Fernández, E. Martín-Zamora, C. Pareja, *Tetrahedron Lett.* **1996**, *37*, 5787; e) R. Fernández, E. Martín, C. Pareja, J. Vázquez, E. Díez, A. Monge, J. M. Lassaletta, *Angew. Chem.* **1998**, *110*, 3598; *Angew. Chem. Int. Ed.* **1998**, *37*, 3428; f) D. Enders, J. Vázquez, G. Raabe, *Chem. Commun.* **1999**, 701.

[8] The cycloaddition reaction of phenoxyketene with ketone hydrazones to give racemic 1-amino β-lactams has been reported. Surprisingly, no yields were included: S. D. Sharma, S. B. Pandhi, *J. Org. Chem.* **1990**, *55*, 2196.

[9] J. K. Whitesell, *Chem. Rev.* **1989**, *89*, 1581.

[10] In contrast with **1a–e**, hydrazone **1f** failed in the 1,2 addition to trifluoromethyl ketones: C. Pareja, E. Martín-Zamora, R. Fernández, J. M. Lassaletta, *J. Org. Chem.* **1999**, *64*, 8846. In addition, ab initio calculations predict an almost perfect planar geometry for the hydrazone moiety in the transition states corresponding to the addition of *N,N*-dialkylhydrazones to π-electrophiles: R. R. Pappalardo, J. M. Muñoz, R. Fernández, J. M. Lassaletta, unpublished results.

[11] A. Defoin, A. Brouillard-Poichet, J. Streith, *Helv. Chim. Acta* **1991**, *74*, 103.

[12] a) S. G. Amin, R. D. Glazer, M. S. Manhas, *Synthesis* **1979**, 210; b) G. I. Georg, P. M. Manshava, X. Guan, *Tetrahedron Lett.* **1991**, *32*, 581.

[13] D. A. Evans, E. B. Sjogren, *Tetrahedron Lett.* **1985**, *26*, 3783.

[14] M. J. Burk, J. E. Feaster, *J. Am. Chem. Soc.* **1992**, *114*, 6266.

[15] B. S. Thyagarajan, *Mechanism of Molecular Migration*, *Vol. 2*, Wiley, New York, **1967**, p. 249.

[16] The scope and mechanistic aspects of this novel reaction are currently under study in our laboratory.

[17] Crystal data for (*R*,*S*)-**3e**: Suitable crystals were obtained from Et$_2$O/cyclohexane at 4°C. C$_{20}$H$_{27}$N$_3$O$_6$, $M_r = 405.45$, crystal size $0.06 \times 0.18 \times 0.20$ mm, orthorhombic, space group P2$_1$2$_1$2$_1$, $a = 7.557(2)$, $b = 14.066(4)$, $c = 19.945(5)$ Å, $V = 2120.2(10)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.270$ g cm^{-3}, $2.50° < \Theta < 20.79°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K. 3856 reflections collected, 2104 were independent [$I > 2\delta(I)$]; 266 parameters, $R = 0.0774$ ($wR = 0.1291$). The crystal was mounted in a CCD diffractometer equipped with a low temperature device and a normal focus, 2.4 kW sealed tube X-ray source operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of two exposure sets, using w scan over the range $3 < \theta < 22°$. The intensities were corrected for Lorentz and polarization effects. No absorption correction. The structure was solved by Multan and Fourier methods. Full matrix least-square refinement was carried out minimizing $w(F_o^2 - F_c^2)^2$. Hydrogen atoms were included in their calculated positions. Refinement on F^2 for all reflections. Weighted R factors (wR) and all GOFs are based on F^2; conventional R factors are based on F. The configuration of C-3 is based on that known for C-2′ in the auxiliary. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135522. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[18] (*S*)-**13** had $[\alpha]_D^{20} = -20.1$ ($c = 0.8$, CH$_3$OH). Lit.: $[\alpha]_D^{20} = -19.8$ ($c = 1$, CH$_3$OH); D. M. Floyd, A. W. Fritz, J. Pluscec, E. R. Weaver, C. M. Cimarusti, *J. Org. Chem.* **1982**, *47*, 5160.

A Highly Conductive Macrocycle-Linked Metallophthalocyanine Polymer**

Richard P. Kingsborough and Timothy M. Swager*

Phthalocyanines are among the most extensively investigated chemical species because of their uses in chemical sensors,[1] low-dimensional conductors,[2–6] nonlinear optics,[7] liquid crystals,[8–12] as well as their utility as catalysts and dyes.[13] Clearly, these properties are derived from the exceptional stability and delocalized electronic nature of the macrocycle. The vast majority of metallophthalocyanine-containing polymers are composed of axially connected phthalocyanines that possess conductivities (σ) of 10^{-3}–10^{-1} S cm^{-1} when oxidatively doped.[5, 14–17] These polymers, however, cannot be exploited for catalytic applications because of the lack of vacant coordination sites. Previous work directed toward the preparation of one- and two-dimensional and macrocycle-linked phthalocyanine polymers resulted in moderately conductive ($\sigma = 10^{-8}$–10^{-2} S cm^{-1}), intractable materials that have not been studied electrochemically.[18–21] Electrochemical polymerization of designed phthalocyanine macrocycles offers a number of advantages over existing systems, including the deposition of thin electroactive films wherein the electronic states of the macrocycle π system mix with those of the polymer backbone. After considering all the desirable attributes that phthalocyanine ligands offer we chose them as ideal moieties from which to design electroactive metal-containing polymers.[22–26] Herein we report the synthesis of a novel highly electroactive polythiophene–metallophthalocyanine hybrid material that exhibits conductivities more than three orders of magnitude higher than previously synthesized macrocycle-connected polymers.

---

[*] Prof. T. M. Swager, R. P. Kingsborough
Department of Chemistry and
Center for Material Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139 (USA)
Fax: (+1) 617-253-8929
E-mail: tswager@mit.edu

[**] Funding from the Office of Naval Research is gratefully acknowledged. This work was supported in part by the MRSEC Program of the National Science Foundation under award number DMR 98–08941.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.