Synthesis of New Chiral Derivatives of *N*,*N*′-Dimethylpropyleneurea (DMPU) and Examination of Their Influence on the Regio- and Enantioselectivity of Addition of 2-(1,3-Dithianyl)lithium to Cyclohex-2-en-1-one

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The preparation of three new chiral derivatives of DMPU (*N*,*N*′-dimethylpropyleneurea) is described (*Schemes 2–4*); one type of derivative carries 1-phenylethyl or 1-cyclohexylethyl groups at the N-atoms of the tetrahydropyrimidin-2(1*H*)-one ring (**2** and **4**), another type of derivative is substituted at C(4) and C(6) of the heterocyclic ring (**7**). The potential of these chiral *Lewis* bases as promoters in the regio- and/or enantioselective addition of 2-(1,3-dithianyl)lithium to cyclohex-2-en-1-one was explored; they are all unable to effect enantioselective addition; the derivatives with branched substituents at the N-atoms do not shift the addition mode from 1,2 to 1,4, while the 3,4,5,6-tetrahydro-1,3,4,6-tetramethylpyrimidin-2(1*H*)-one does (*Scheme 5*). The results provide useful information regarding the nature of the nucleophilic organolithium reagent: obviously, the steric hindrance to Li complexation on the C=O O-atom of the tetrahydropyrimidin-2(1*H*)-one by branched substituents at N-atoms (*cf.* X-ray crystal structure of **2** in the *Fig.*) prevents solvent-separated-ion-pair (SSIP) formation; this was confirmed by PM3 and B3LYP/3-21-G(d)//PM3 calculations (*Scheme 6*).

Introduction. – Hexamethylphosphoric triamide (HMPA) is a highly polar, aprotic solvent that enhances the rates of numerous nucleophilic reactions [1]. Nevertheless, HMPA is a known carcinogen, potentially hazardous for use either in industry or the laboratory. *N*,*N*′-Dimethylpropyleneurea (= 3,4,5,6-tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-one; DMPU) has been shown to be an excellent, nonmutagenic, and safe replacement for HMPA [2]. Tetraalkylsulfamides [3] and quinuclidine *N*-oxide [4] have also been proposed as substitutes for HMPA.

Recently, *Denmark et al.* [5] examined the effectiveness of *chiral derivatives of HMPA* as *Lewis* base promoters[2])[3]) in several enantioselective reactions, including the so-called desymmetrization of *meso*-epoxides and aldol additions (*Scheme 1*, *Eqns. 1* and *2*).

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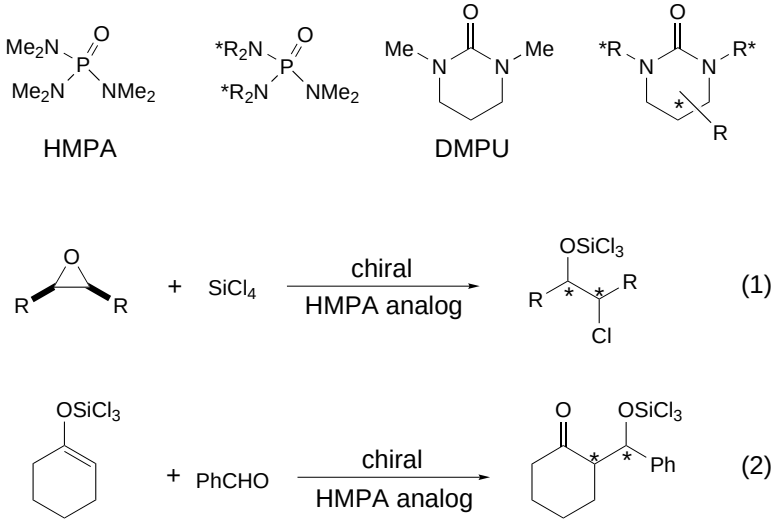
[1]) Part of the Ph. D. Thesis of *M.H.*, Dissertation No. 10352, ETH-Zurich, 1993.

[2]) For a review article on organic catalysts, see [6].

[3]) Analogous phosphonamide catalysts were very recently reported by *Buono et al.*, but the results could not be reproduced [7].

Scheme 1. *HMPA and DMPU, and Their Chiral Analogs in Enantioselective Reactions*



Motivated by *Denmark*'s work, we deemed it of interest to explore the potential of *chiral derivatives of DMPU* as enantioselective promoters in the addition of 2-(1,3-dithianyl)lithium to cyclohex-2-en-1-one to give either the 1,2- or 1,4-adduct, which are both chiral.

Results and Discussion. – *Synthesis of Chiral Analogs of DMPU.* C_2-Symmetrical diamines (*R*,*R*)-**1** and (*S*,*S*)-**1** were prepared from 1,3-dichloropropane and (*R*)- or (*S*)-1-phenylethylamine[4])[5]), respectively, according to the procedure of *Feringa et al.* [10]. Subsequent reaction with triphosgene [11] produced the desired chiral DMPU analogs (*R*,*R*)-**2** and (*S*,*S*)-**2** (*Scheme 2*)[6]). Recrystallization of (*R*,*R*)-**2** afforded single crystals suitable for X-ray analysis (see *Fig.*). Most interesting is the propeller-like orientation of the 1-phenylethyl groups, which should lead to high enantioselectivities in reactions taking place with suitable substrates coordinated to the C=O O-atom [13]. The solid-state conformation adopted by (*R*,*R*)-**2** (*Fig.*) is readily explained as a consequence of allylic $A^{1,3}$ strain, which would be present in the other possible conformations around the N–CHMePh bond [14]. This qualitative conclusion is supported by theoretical calculations summarized in the *Table.*

Diamine (*R*,*R*)-**3** was obtained in good yield from the reaction of commercial (*R*)-1-cyclohexylethylamine and acrolein, followed by reduction with $NaBH_4$ [16]; cyclization with carbonyldiimidazole gave the DMPU analog (*R*,*R*)-**4** ('dodecahydro-**2**'; *Scheme 3*).

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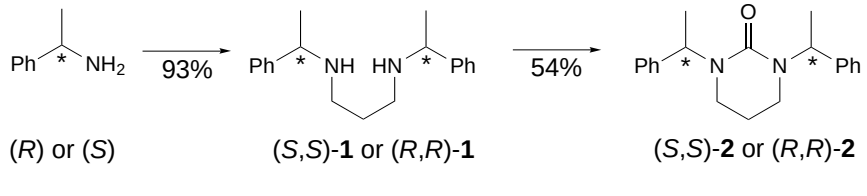
[4]) For recent reviews on applications of 1-phenylethylamine in the preparation of enantiomerically pure compounds, see [8].

[5]) For *N*-monoalkylations of 1-phenylethylamine in DMPU solution, see [9].

[6]) The moderate yield encountered in the cyclization reaction is a consequence of oligomer formation [12].

Scheme 2. *Preparation of the Chiral DMPU Analogs (*S,S*)-***2** *and (*R,R*)-***2** *from (*S*)- and (*R*)-1-Phenylethylamine*



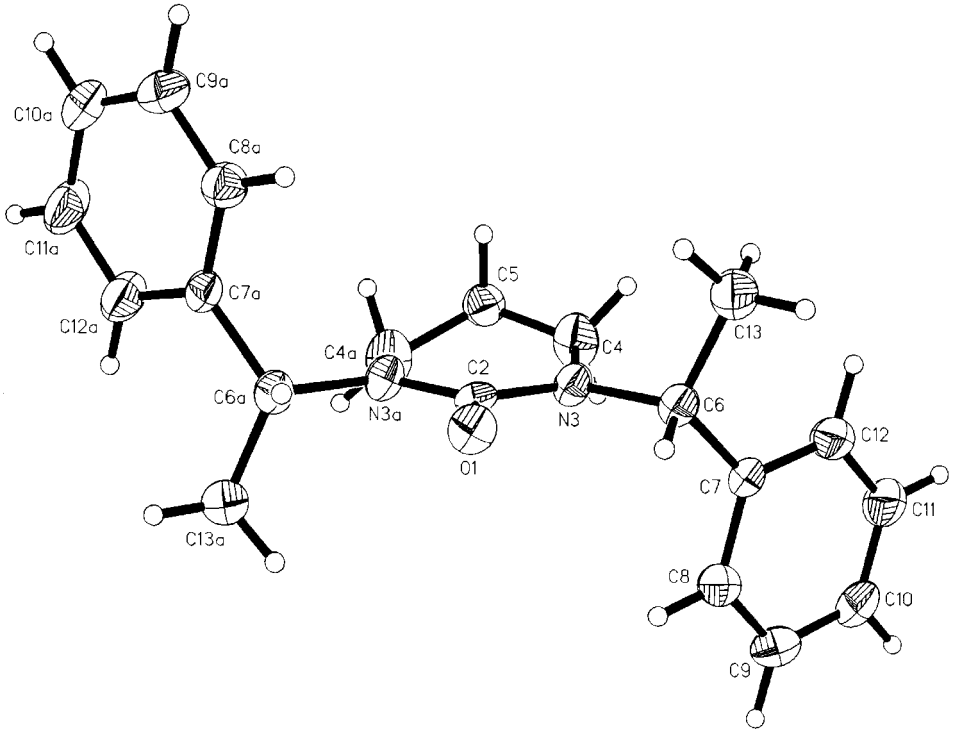


Figure. *X-Ray crystal structure of the chiral DMPU analog (*R,R*)-***2** (the crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre*, No. CCDC 177735)

Finally, the chiral DMPU derivatives (*R*,*R*)-**7** and (*S*,*S*)-**7**, with stereogenic centers in the heterocyclic ring, rather than on the *N*-substituents, were prepared from acetylacetone as depicted in *Scheme 4*. 1,3-Dioxime **5** was obtained in good yield, and reduction with *Raney*-Ni provided a mixture of *meso*- and *rac*-diamines **6** [17]. The undesired *meso*-diastereoisomer was readily separated by flash-column chromatography, and *rac*-**6** was resolved by fractional crystallization of the dibenzoyl tartrate salt [18]. Finally, cyclization with phosgene and *N*-methylation under *Leuckart-Wallach* conditions [19] afforded (*R*,*R*)-**7** and (*S*,*S*)-**7** (*Scheme 4*).

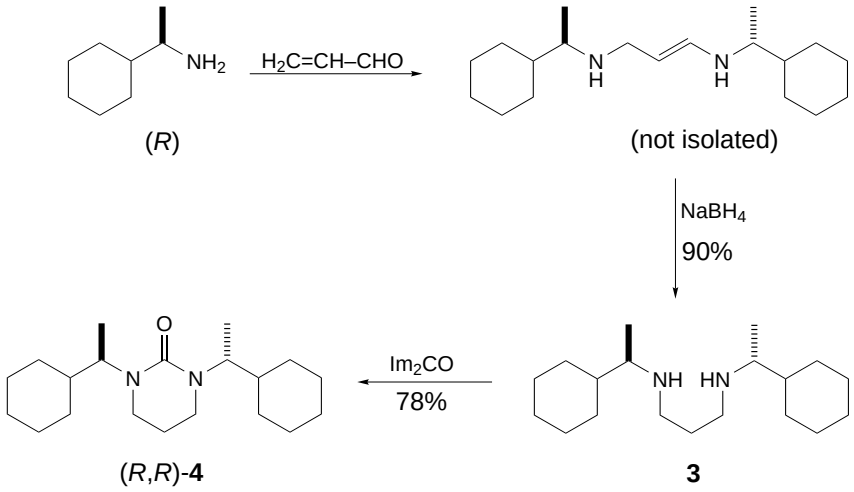
Addition of 2-(1,3-Dithianyl)lithium to Cyclohex-2-en-1-one in the Presence of **2**, **4** *and* **7**. We examined the regio- and enantioselectivity of addition of 2-(1,3-dithianyl)lithium

Table. *Calculated (Gas-Phase) Conformational Preference of the* N-*(1-Phenylethyl)* N-*Substituents in (*R,R*)-***2** [15]

A **B**

Method	ΔE [kcal/mol] (**A** → **B**)
HF/6-311 + G(d,p)//HF/6-31G(d)	+ 2.35
B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d)	+ 2.59

Scheme 3. *Preparation of the Chiral DMPU Analog (*R,R*)-***4** *from (*R*)-1-Cyclohexylethylamine* (Im = imidazol-1-yl)

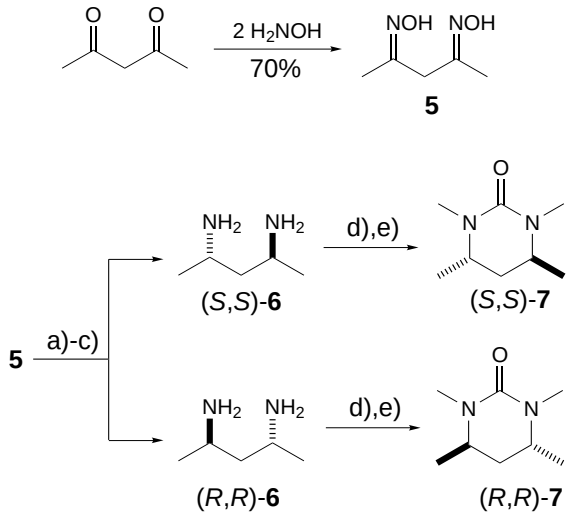


to cyclohex-2-enone, both in the absence and presence of *Lewis* base promoters (*Scheme 5*). As expected [19], in the absence of HMPA or DMPU, the predominant mode of reaction is 1,2-addition (→ **8**). When HMPA or DMPU is added (*Entries 2* and *3* in *Scheme 5*) the 1,4-adduct **9** becomes the main product. Product **9** is also the major regioisomer in the presence of chiral urea (*S*,*S*)-**7** (*Entry 6*) but, to our surprise, product **8** of 1,2-addition is highly predominant in the presence of (*S*,*S*)-**2** or (*R*,*R*)-**4** (*Entries 4* and *5*)[7]).

According to the models of *Dolak* and *Bryson* [20a], *Cohen et al.* [20b], and *Sikorski* and *Reich* [20c], the regioselectivity of nucleophile addition to enones is a function of the ion-pair structure of the Li reagent, where contact-ion pairs (CIP) with a

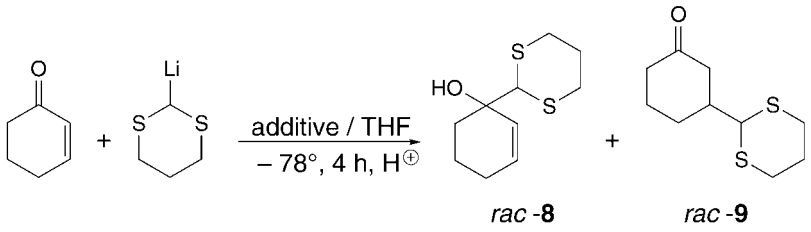
[7]) It has been established that the addition of 2-(1,3-dithianyl)lithium to cyclohex-2-en-1-one is irreversible [19d].

Scheme 4. *Preparation of the Chiral DMPU Analogs (*S,S*)-***7** *and (*R,R*)-***7** *from Acetylacetone*



a) *Raney*-Ni, NaOH. b) Flash column chromatography. c) Resolution with dibenzoyl tartaric acid. d) Phosgene. e) Aq. H_2CO/HCO_2H

Scheme 5. *Addition of 2-(1,3-Dithianyl)lithium to Cyclohex-2-en-1-one.* Both adducts are racemic in all cases, as determined by HPLC analysis on a teicoplanin (*Chirobiotic T*™) column and/or optical-rotation measurement. The diastereoisomer ratio was determined by integration of corresponding signals in the ^{1}H-NMR spectra.



Entry	Additive (2 equiv.)	Ratio **8** / **9**
1	-----	99 : 1
2	HMPA	9 : 91
3	DMPU	25 : 75
4	(*S,S*)-**2**	99 : 1
5	(*R,R*)-**4**	99 : 1
6	(*S,S*)-**7**	17 : 83

tight C–Li association give 1,2-addition, whereas solvent-separated ion pairs (SSIP) give predominantly 1,4-addition. In the system at hand, the contrasting effect of HMPA and DMPU (giving 1,4-addition), and chiral derivatives **2** and **4** (affording 1,2-addition) imply that the latter are unable to form complexes with the cation, probably due to steric hindrance by the *N*-(1-phenylethyl) or *N*-(1-cyclohexylethyl) groups. Thus, CIP 2-(1,3-dithianyl)lithium, with an intact C–Li association[8]), adds to the C=O moiety with negligible enantioselectivity (*Entries 4* and *5* in *Scheme 5*).

By contrast, chiral DMPU derivative (*S*,*S*)-**7** is obviously able to coordinate to the Li-atom, so that an SSIP is formed, and the dithianyl nucleophile adds mainly in the 1,4-fashion (*Entry 6* in *Scheme 5*).

Nevertheless, product **9** is racemic, indicating that the stereogenic centers in (*S*,*S*)-**7** are too far remote from the coordinating site to induce significant enantioselectivity of the reaction. In an alternative interpretation, a 'naked' carbanionic 2-(1,3-dithianyl) species may be considered to add to cyclohex-2-en-1-one, with no effective participation of the chiral Li-solvate in the transition state.

Computational Studies. A computational investigation was undertaken to gain support for the speculative statements advanced in the previous section. The main question is whether 2-(1,3-dithianyl)lithium is present as SSIP in THF/HMPA and THF/DMPU solutions, but as CIP species in THF solution. To be able to keep the model system as authentic as possible, with the available amount of computational resources, we chose a combined semiempirical and density-functional approach. The semiempirical PM3 method [22] with Li parameters of *Anders et al.* [23] has been widely used in organolithium chemistry [24], and it has been shown to adequately reproduce geometries of organolithium compounds; however, the energies obtained by the PM3 method are usually not as accurate [25]. Recently, *Abbotto*, *Streitwieser*, and *Schleyer* have demonstrated that energies obtained by means of density-functional theory with the B3LYP hybrid function with standard basis sets [6-31 + G(d), 6-311 + G(d)] on the PM3-optimized geometries (B3LYP/6-31 + G(d)//PM3) produce high-level results (B3LYP/6-31 + G(d)//B3LYP/6-31G(d)) of high accuracy [26]. Thus, we applied this B3LYP//PM3 method for our calculations.

Cryoscopic measurements in THF have demonstrated that (2-(1,3-dithianyl)lithium is monomeric in solution at low temperature [27], and it is well-established that the most stable and common coordination sphere of Li is tetrahedral [28]. Therefore, the energy associated with equilibria depicted in *Scheme 6* was calculated at the B3LYP/3-21G(d) level of theory with PM3-optimized geometries for the involved species and ligand molecules. The most relevant result is that, in the presence of coordinating (L = HMPA or DMPU), solvation of the Li^+ cation to give an SSIP 2-(1,3-dithianyl) carbanion is a highly exothermic (favorable) process (*Entries 2* and *3* in *Scheme 6*). By contrast, when L is THF or the chiral DMPU analog **2**, formation of SSIP species is calculated to be an endothermic (unfavorable) process (*Entries 1* and *4*). These computational results are in line with the experimentally observed results discussed in the previous section.

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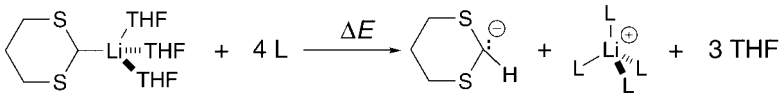
[8]) For crystal structures of Li dithianes, see [21].

Scheme 6. *Calculated Energies for Lithium Cation Solvation and Concomitant Formation of SSIP Species* (CIP = contact ion pair, SSIP = solvent-separated ion pair, L = coordinating solvent THF, HMPA, DMPU, or (*S*,*S*)-**2**)



Entry	L	Δ*E* [kcal/mol]
1	THF	+14.8
2	HMPA	−39.6
3	DMPU	−14.2
4	(*S*,*S*)-**2**	+0.7

Conclusions. – The observations reported are best interpreted by assuming that the DMPU derivatives **2** and **4** are unable to associate with the cation of 2-(1,3-dithianyl)lithium, leading to nonenantioselective 1,2-addition products. In contrast, (*R*,*R*)-**7** effectively solvates Li^+ so that the organic anion adds to cyclohex-2-en-1-one in a 1,4-fashion. The fact that no enantioselectivity was detected in this reaction is an indication that the chiral promoter is not intimately involved in an enantioface-differentiating step.

Experimental Part

General. Flasks, stirring bars, and hypodermic needles used for the generation and reactions or organolithiums were dried for *ca*. 12 h at 120° and allowed to cool in a desiccator over anh. $CaSO_4$. Anh. THF was obtained by distillation from benzophenone ketyl. DMPU and HMPA were dried over CaH_2 and then distilled at reduced pressure. 1,3-Dithiane was sublimed before use. The BuLi employed was titrated according to the method we developed [29]. TLC: *Merck DC-F*$_{254}$ plates, detection by UV light. Flash column chromatography (FC): *Merck* silica gel (0.040–0.063 mm). HPLC: *Waters 600* instrument fitted with UV/VIS detector, and a chiral stationary phase of teicoplanin (*Chirobiotic T*™) for the determination of enantiomeric ratios. M.p.: not corrected. ^{1}H-NMR Spectra: *Jeol Eclipse-400* (400 MHz), *Bruker Ultra Shield* (300 MHz), and *Jeol GSX-270* (270 MHz) spectrometers. ^{13}C-NMR Spectra: *Jeol Eclipse-400* (100 MHz), *Bruker Ultra Shield* (75 MHz), and *Jeol GSX-270* (67.5 MHz). Chemical shifts (δ) in ppm downfield from internal TMS reference; the coupling constants (*J*) are given in Hz. MS: *Hewlett Packard HP-5986* spectrometer. Elemental analyses were obtained from *Galbraith Laboratories, Inc.*, Knoxville, TN.

*(*R,R*)- and (*S,S*)-*N,N′*-Bis(1-phenylethyl)propane-1,3-diamine* ((*R*,*R*)- and (*S*,*S*)-**1**). The procedure described by *Feringa et al*. [10] was followed, with 11.77 g (97.2 mmol) of (*R*)- or (*S*)-1-phenylethylamine and 3.07 ml (32.4 mmol) of 1,3-dichloropropane: (*R*,*R*)-**1**: 94% yield. $[\alpha]_D^{20} = +65.4$ ($c = 2.4$, $CHCl_3$). ([10]: $[\alpha]_D^{20} = -66.3$ ($c = 0.55$, $CHCl_3$) for the (*S*,*S*) enantiomer). (*S*,*S*)-**1**: 93% yield. $[\alpha]_D^{20} = -66.8$ ($c = 4.2$, $CHCl_3$). ([10]: $[\alpha]_D^{20} = -66.3$ ($c = 0.55$, $CHCl_3$)).

*(*R,R*)- and (*S,S*)-3,4,5,6-Tetrahydro-1,3-bis(1-phenylethyl)pyrimidin-2(1*H*)-one* ((*R*,*R*)- and (*S*,*S*)-**2**). The starting diamine ((*R*,*R*)-**1** or (*S*,*S*)-**1**; 7.12 g, 25.2 mmol), Et_3N (7.02 ml, 50.4 mmol), and 250 ml of dry CH_2Cl_2 were placed in a round-bottom flask, and the resulting mixture was cooled to 0° before the dropwise addition of a soln. of 2.65 g (8.9 mmol) of triphosgene in 150 ml of CH_2Cl_2 for 2 h. Stirring was continued at 0° for 3 h and then at r.t. for 2 d. Then, 200 ml of 1N HCl was added at 0°, the aq. phase was separated and extracted with two 100-ml portions of CH_2Cl_2, the combined org. phases were washed with brine soln., dried (Na_2SO_4), and concentrated. The product was purified by FC (petroleum ether/AcOEt 9:1).

*Data of (*S,S*)-***2***:* 45% yield. M.p. 124–125°. $[\alpha]_D^{20} = -125.5$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.55 (*d*, *J* = 7.1, 6 H); 1.67–1.80 (*m*, 2 H); 2.72–2.80 (*m*, 2 H); 3.00–3.08 (*m*, 2 H); 6.05 (*q*, *J* = 7.1, 2 H); 7.20–7.40 (*m*, 10 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 16.3; 22.8; 39.9; 51.7; 127.3; 128.0; 128.7; 142.1; 156.4. MS (20 eV): 308 (M^+), 293, 204, 203, 189, 162, 146, 120, 105, 91, 41. Anal. calc. for $C_{20}H_{24}N_2O$ (308.43): C 77.89, H 7.84, N 9.08; found: C 77.84, H 7.88, N 9.11.

*Data of (*R,R*)-***2***:* 46% yield. M.p. 124–125°. $[\alpha]_D^{20} = +125.5$ ($c = 1$, $CHCl_3$).

*(*R,R*)-N,N′-Bis(1-cyclohexylethyl)propane-1,3-diamine* ((*R*,*R*)-**3**). A mixture of 44 ml (0.3 mol) of (*R*)-1-cyclohexylethylamine, 60 ml (0.44 mol) of Et_3N, and 8.0 g of K_2CO_3 was treated (dropwise addition) with 10.0 ml (0.15 mol) of acrolein at 4°. The mixture was stirred for 3 h in an ice-bath, filtered over *Celite*, and the collected solid material washed with 75 ml of MeOH. The filtrate was then treated with 8.36 g (0.23 mol) of $NaBH_4$ in 75 ml of MeOH at 4°, and stirring was continued at r.t. for 1 h. The mixture was heated to 50° for 2 h, and then concentrated at r.t. The residue was rinsed with 100 ml of H_2O and extracted with three 50-ml portions of Et_2O. The combined org. extracts were dried ($MgSO_4$) and concentrated in the rotary evaporator to give 40.6 g (90% yield) of (*R*,*R*)-**3** as a yellow oil. This product was characterized as the corresponding hydrochloride (**3**·2 HCl). $[\alpha]_D^{25} = +8.8$ ($c = 0.625$, H_2O). IR ($CHCl_3$): 3420, 2930, 2860, 2740, 1590, 1450, 1390, 1050. ^{1}H-NMR ($CDCl_3$/D_2O, 200 MHz): 3.31–3.07 (*m*, 6 H); 2.12 (*dt*, *J* = 7.5, 2 H); 1.9–1.6 (br, 12 H); 1.4–1.05 (br, 10 H); 1.3 (*d*, *J* = 7.5, 6 H). Anal. calc. for $C_{19}H_{40}Cl_2N_2$ (367.45): C 62.11, H 10.97, N 7.62; found: C 61.83, H 10.82, N 7.52.

*(*R,R*)-1,3-Bis(1-cyclohexylethyl)-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one* ((*R*,*R*)-**4**). A soln. of 6.0 g (20 mmol) of (*R*,*R*)-**3** in 50 ml of THF was treated with 4.0 g (24 mmol) of carbonyldiimidazole at 4° (ice-bath). The mixture was stirred at r.t. for 12 h, cooled to 4° (ice bath), and treated with 100 ml of 1N HCl. The resulting mixture was extracted with three 100-ml portions of CH_2Cl_2, the combined org. extracts were dried ($MgSO_4$), and concentrated in the rotary evaporator to afford 5.0 g (78% yield) of (*R*,*R*)-**4** as yellowish crystals, which were recrystallized from *t*-BuOMe. M.p. 72–75°. $[\alpha]_D^{25} = -17.0$ ($c = 1.34$, $CHCl_3$). IR ($CHCl_3$): 3370, 2980, 2830, 1700, 1650, 1600, 1500, 1450, 1380, 1170, 850. ^{1}H-NMR ($CDCl_3$, 300 MHz): 4.27 (*dt*, $^1J = 7$, $^2J = 3$, 2 H); 3.1 (*dt*, $^1J = 12$, $^2J = 6$, 2 H); 1.87 (*quint.*, 2 H); 1.75–1.6 (*m*, 10 H); 1.3–0.9 (*m*, 12 H); 1.07 (*d*, *J* = 7, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 156.0; 54.0; 40.6; 39.2; 30.4; 30.0; 26.4; 26.3; 26.2; 22.6; 16.0. Anal. calc. for $C_{20}H_{36}N_2O$ (320.52): C 74.95, H 11.32, N 8.74; found: C 74.64, H 11.41, N 8.63.

*(4*S*,6*S*)-3,4,5,6-Tetrahydro-1,3,4,6-tetramethylpyrimidin-2(1*H*)-one* ((*S*,*S*)-**7**). (*S*,*S*)-Pentane-2,4-diamine dihydrochloride [18] (32.1 g, 1.83 mmol) in 300 ml of toluene was added to 95 ml of H_2O. The resulting suspension was vigorously stirred at 4° (ice bath) before the dropwise addition of 337 ml of 4.5N NaOH (1.5 mol) and 345 ml of a 20% soln. of phosgene in toluene (575 mmol). Stirring was continued for 4 h at r.t., and then solvents were removed in a rotary evaporator. The residue was treated with 56.5 ml of 36% aq. soln. of HCHO (732 mmol) and 188 ml of 98% HCOOH (5 mol). The mixture was heated under reflux for 12 h, and then concentrated in the rotary evaporator. Compound (*S*,*S*)-**7** (21.1 g, 74%) was obtained by distillation (b.p. 102°/1.5 mbar) over CaH_2. Colorless oil. $[\alpha]_D^{25} = +11.0$ ($c = 1.18$, $CHCl_3$). IR (film): 3530, 2970, 1630, 1500, 1450, 1150. ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.37 (*ddq*, $^1J = 6.4$, $^2J = {}^3J = 6.0$, 2 H); 2.86 (*s*, 6 H); 1.76 (*dd*, 2 H); 1.15 (*d*, 6 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 156.3; 49.3; 36.8; 33.0; 10.6.

General Procedure for the Addition of 2-(1,3-Dithianyl)lithium to Cyclohex-2-en-1-one. A soln. of 0.12 g (1.0 mmol) of 1,3-dithiane in 10 ml of dry THF was cooled to −78° under N_2 before the dropwise addition of 0.4 ml of BuLi in hexane (2.4M, 1.0 mmol). The resulting mixture was stirred at −78° for 15 min and at 0° for 1 h, cooled again to −78°, and treated with chiral urea (1.0 mmol) in 15 ml of THF. Stirring was continued for 25 min at −78°, and then the soln. was transferred *via* cannula to a flask containing 0.1 ml (1.0 mmol) of cyclohex-2-en-1-one in 5 ml of THF, also at −78°. The mixture was stirred at this temp. for 4 h, before it was quenched with 3 ml of sat. aq. NH_4Cl soln. The THF was removed at reduced pressure, and the residue was partitioned between H_2O and CH_2Cl_2. The org. phase was extracted with two portions of CH_2Cl_2, the combined org. extracts were washed with 40 ml of H_2O, dried, and concentrated. Final purification was accomplished by FC (hexane/AcOEt, 92:8). *1,2-Adduct: 1-(1,3-Dithian-2-yl)cyclohex-2-en-1-ol* (**8**): ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.60–2.10 (*m*, 8 H); 2.30–2.38 (br., 1 H); 2.78–2.91 (*m*, 4 H); 4.20 (*s*, 1 H); 5.68–5.73 (*m*, 1 H); 5.89–5.93 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 18.6; 25.1; 25.9; 30.6; 30.8; 33.0; 59.8; 71.8; 129.4; 132.4. MS (20 eV): 216 (M^+), 199, 119, 97, 79, 55, 41.

1,4-Adduct: 3-(1,3-Dithian-2-yl)cyclohexan-1-one (**9**): ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.41–1.60 (*m*, 2 H); 1.63–1.76 (*m*, 1 H); 1.90–2.44 (*m*, 8 H); 2.72–2.75 (*m*, 4 H); 3.95 (*d*, *J* = 5.1, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 24.7; 26.1; 28.4; 30.6; 41.1; 43.4; 45.1; 53.3; 210.1. MS (20 eV): 216 (M^+), 142, 119, 110, 91, 79, 55, 41.

These spectroscopic data are similar to those reported previously by us [2a].

Financial support from *Conacyt*, México, *via* grant 33023-E is gratefully acknowledged. We are also indebted to the reviewers and to Profs. *Scott E. Denmark*, University of Illinois, and *Patrick J. Walsh*, University of Pennsylvania, for useful comments. We thank *A. K. Beck* and *D. Kalbermatter* for help in producing the manuscript of this paper.

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Received March 9, 2002