

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.

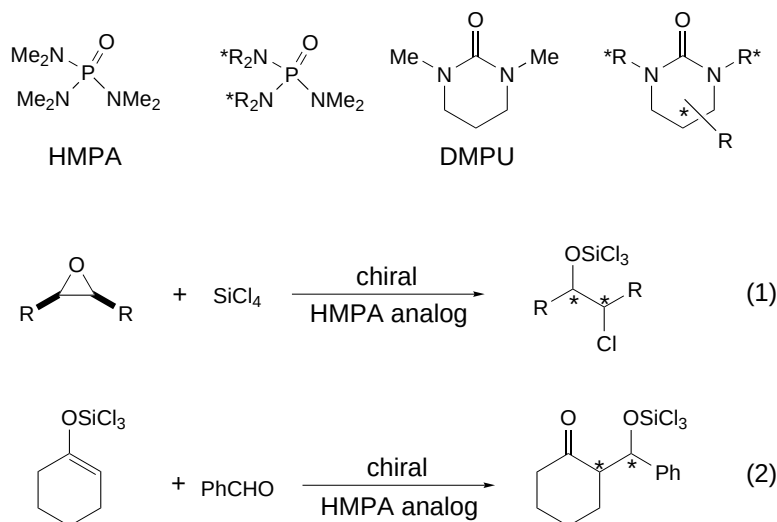
Recently, Denmark *et al.* [5] examined the effectiveness of *chiral derivatives of HMPA as Lewis base promoters*²⁾³⁾ in several enantioselective reactions, including the so-called desymmetrization of *meso*-epoxides and aldol additions (Scheme 1, Eqns. 1 and 2).

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.

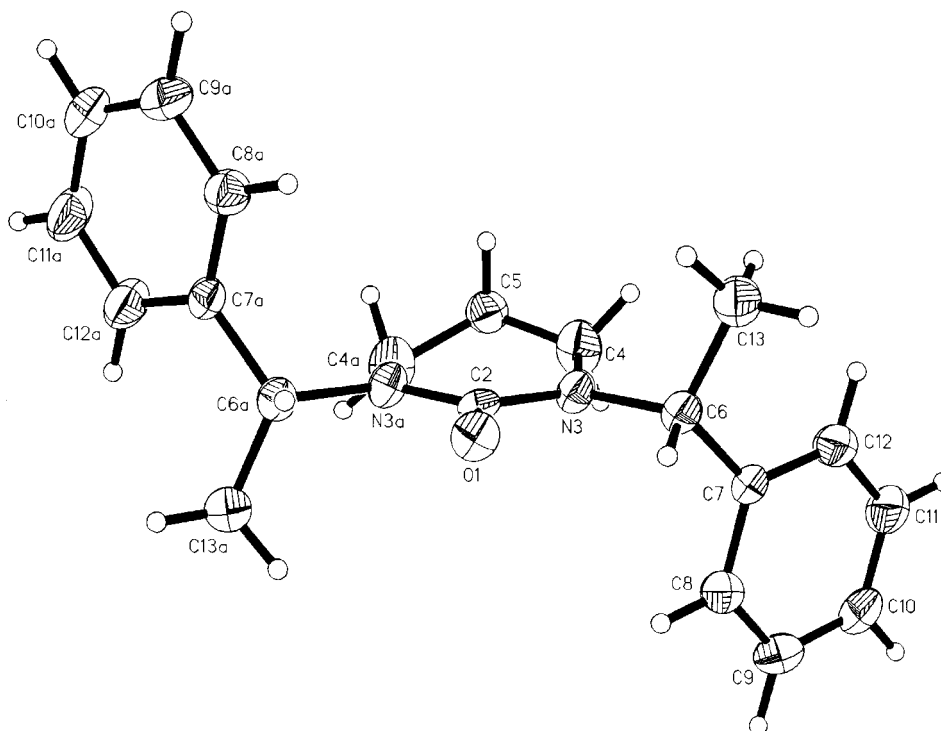
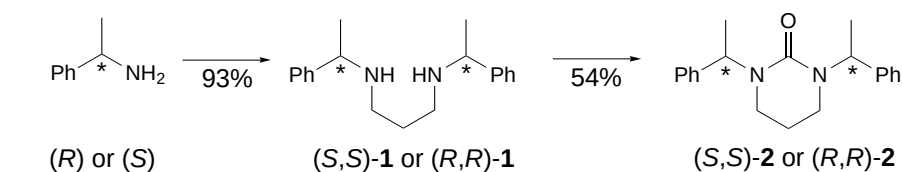
Results and Discussion. – *Synthesis of Chiral Analogs of DMPU.* C_2 -Symmetrical diamines (*R,R*)-**1** and (*S,S*)-**1** were prepared from 1,3-dichloropropane and (*R*)- or (*S*)-1-phenylethylamine⁴⁾⁵⁾, respectively, according to the procedure of *Feringa et al.* [10]. Subsequent reaction with triphosgene [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).

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].

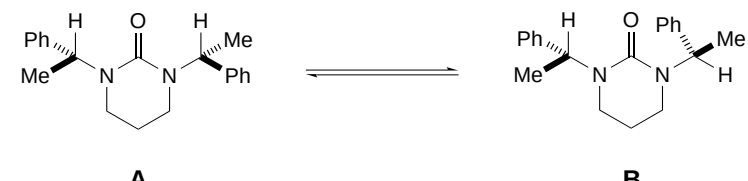
6) The moderate yield encountered in the cyclization reaction is a consequence of oligomer formation [12].

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

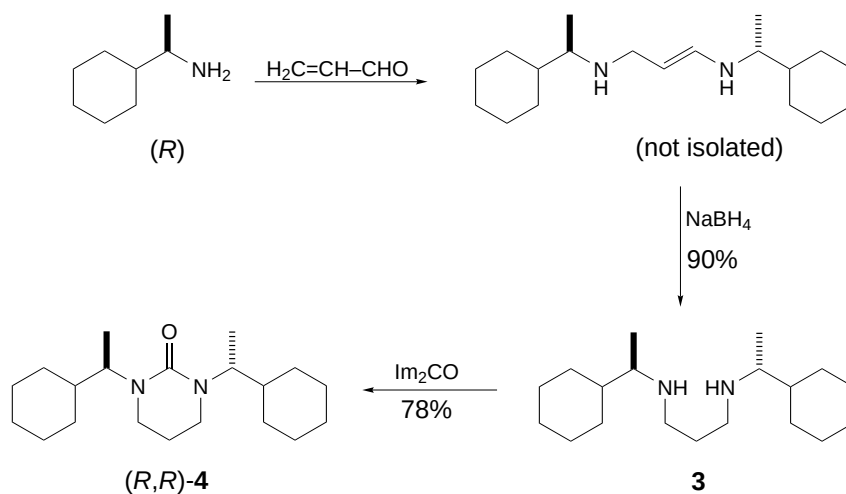
Addition of 2-(1,3-Dithianyl)lithium to Cyclohex-2-en-1-one in the Presence of **2**, **4** and **7**. We examined the regio- and enantioselectivity of addition of 2-(1,3-dithianyl)lithium

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



Method	ΔE [kcal/mol] (A $\rightarrow$ 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)

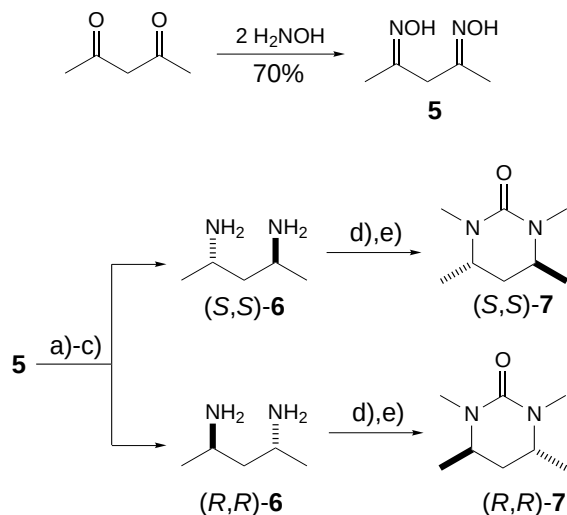


to cyclohex-2-enone, both in the absence and presence of *Lewis* base promoters (Scheme 5). As expected [19], in the absence of HMPA or DMPU, the predominant mode of reaction is 1,2-addition ($\rightarrow$ **8**). When HMPA or DMPU is added (Entries 2 and 3 in Scheme 5) the 1,4-adduct **9** becomes the 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

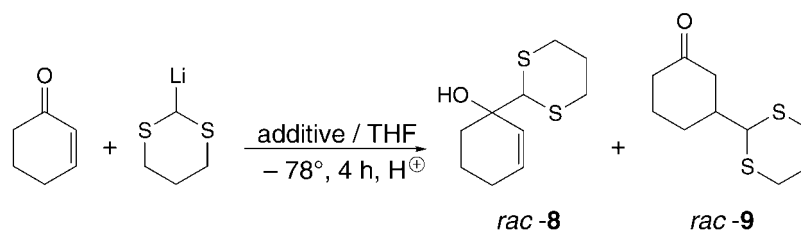
⁷⁾ It has been established that the addition of 2-(1,3-dithianyl)lithium to cyclohex-2-en-1-one is irreversible [19d].

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. $\text{H}_2\text{CO}/\text{HCO}_2\text{H}$

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*TM) column and/or optical-rotation measurement. The diastereoisomer ratio was determined by integration of corresponding signals in the ¹H-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 association⁸⁾, 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*).

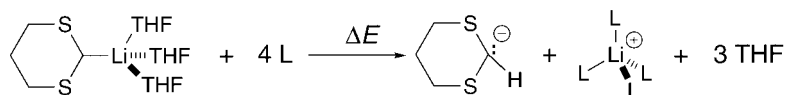
Nevertheless, product **9** is racemic, indicating that the stereogenic centers in (*S,S*)-**7** are too far remote from the coordinating site to induce significant enantioselectivity of the reaction. In an alternative interpretation, a ‘naked’ carbanionic 2-(1,3-dithianyl) species may be considered 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.

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	ΔE [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-F₂₅₄* 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 TTM*) for the determination of enantiomeric ratios. M.p.: not corrected. ^1H -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. $[\alpha]_{\text{D}}^{20} = +65.4$ (*c* = 2.4, CHCl_3). ([10]: $[\alpha]_{\text{D}}^{20} = -66.3$ (*c* = 0.55, CHCl_3) for the (*S,S*) enantiomer). (*S,S*)-**1**: 93% yield. $[\alpha]_{\text{D}}^{20} = -66.8$ (*c* = 4.2, CHCl_3). ([10]: $[\alpha]_{\text{D}}^{20} = -66.3$ (*c* = 0.55, CHCl_3)).

(*R,R*)- and (*S,S*)-3,4,5,6-Tetrahydro-1,3-bis(1-phenylethyl)pyrimidin-2(1H)-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). $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}$ (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 ($3 \cdot 2 \text{HCl}$). $[\alpha]_D^{25} = +8.8$ ($c = 0.625$, H_2O). IR (CHCl_3): 3420, 2930, 2860, 2740, 1590, 1450, 1390, 1050. $^1\text{H-NMR}$ ($\text{CDCl}_3/\text{D}_2\text{O}$, 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 $\text{C}_{19}\text{H}_{40}\text{Cl}_2\text{N}_2$ (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(1H)-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. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{20}\text{H}_{36}\text{N}_2\text{O}$ (320.52): C 74.95, H 11.32, N 8.74; found: C 74.64, H 11.41, N 8.63.

(4S,6S)-3,4,5,6-Tetrahydro-1,3,4,6-tetramethylpyrimidin-2(1H)-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. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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)*: $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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): $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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].

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